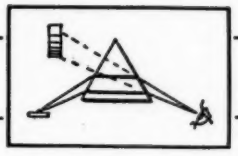
Journal of the OPTICAL SOCIETY *of* AMERICA

VOLUME 33
No. 4



APRIL
1943

Spectrochemical Light Source Errors and Their Compensation . . . . . H. H. GROSSMAN, R. A. SAWYER, AND H. B. VINCENT 185

Spectral Characteristics of Optical Wedges . . . . . MONROE H. SWEET 194

Ultraviolet Absorption Spectra of Protein Solutions . R. NORMAN JONES AND HUGH J. CREECH 209

New Spectroscopic Source Unit . . . . . M. F. HASLER AND H. W. DIETERT 218

Measurement of Transmission and Contrast in Optical Instruments . . . . . D. B. MCRAE 229

Optical Society of America, Incorporated, Notice of Election of Officers 244

Letters to the Editor:

Magnification and Brightness of Images on the Retina . . . . . FRANK BENFORD 245

Comment on "Meetings of Scientific Societies in Wartime" . . . . . V. G. W. HARRISON 245

Published monthly
at Prince and Lemon Sts., Lancaster, Pa.
by the
AMERICAN INSTITUTE OF PHYSICS
Incorporated
175 Fifth Avenue, New York, N. Y.
FOR AND UNDER THE EDITORIAL SUPERVISION OF THE
OPTICAL SOCIETY OF AMERICA

BOSTON UNIVERSITY
COLLEGE OF LIBERAL ARTS
LIBRARY

THE OPTICAL SOCIETY OF AMERICA

Officers of the Society

A. G. WORTHING, *President*
University of Pittsburgh
Pittsburgh, Pennsylvania

A. H. PFUND, *Vice President*
Johns Hopkins University
Baltimore, Maryland

ARTHUR C. HARDY, *Secretary*
Massachusetts Institute of Technology
Cambridge, Massachusetts

W. W. GRAEPER, *Treasurer*
Bausch & Lomb Optical Company
Rochester, New York

The Board of Directors consists of the above officers; the Editor of the Journal; the Past President; and five directors-at-large.

K. S. GIBSON, *Past President*
National Bureau of Standards
Washington, D. C.

GEORGE R. HARRISON, *Editor*
Massachusetts Institute of Technology
Cambridge, Massachusetts

Directors-at-Large

J. W. BEAMS
University of Virginia
Charlottesville, Virginia

D. B. JUDD
National Bureau of Standards
Washington, D. C.

RUDOLF KINGSLAKE
Eastman Kodak Company
Rochester, New York

D. L. MACADAM
Eastman Kodak Company
Rochester, New York

R. A. SAWYER
University of Michigan
Ann Arbor, Michigan

Rochester, New York, Section

J. H. WEBB, *President*
G. H. AKLIN, *Vice President*
A. F. TURNER, *Secretary*
F. H. PERRIN, *Treasurer*

Councillors:

F. E. ALTMAN
J. W. FORREST
F. M. E. HOLMES
V. L. PARKS
R. B. HORSFALL (*ex officio*)

Patrons

AMERICAN OPTICAL COMPANY — BAUSCH & LOMB OPTICAL COMPANY
EASTMAN KODAK COMPANY

Corporation Members

AMERICAN CYSTOSCOPE MAKERS, INC., New York, New York
AMERICAN OPTICAL COMPANY, Southbridge, Massachusetts
BAUSCH & LOMB OPTICAL COMPANY, Rochester, New York
BELL & HOWELL COMPANY, Chicago, Illinois
BELL TELEPHONE LABORATORIES, INC., New York, New York
BENDIX AVIATION CORPORATION, New York, New York
CORNING GLASS WORKS, Corning, New York
E. I. DUPONT DE NEMOURS & COMPANY, INC., Chemical Department, Experimental Station, Wilmington, Delaware
EASTMAN KODAK COMPANY, Rochester, New York
FAIRCHILD AVIATION CORPORATION, Jamaica, New York
FISH-SCHURMAN CORPORATION, New York, New York
GAERTNER SCIENTIFIC CORPORATION, Chicago, Illinois
W. & L. E. GURLEY, Troy, New York
INTERCHEMICAL CORPORATION, New York, New York
KEUFFEL & ESSER COMPANY, Hoboken, New Jersey
NATIONAL CARBON COMPANY, Cleveland, Ohio
PERKIN-ELMER CORPORATION, Glenbrook, Connecticut
POLAROID CORPORATION, Cambridge, Massachusetts
PORTMAN MACHINE TOOL COMPANY, New Rochelle, New York
SIMPSON OPTICAL MANUFACTURING COMPANY, Chicago, Illinois
SPENCER LENS COMPANY, Buffalo, New York
ARTHUR H. THOMAS COMPANY, Philadelphia, Pennsylvania

THE OPTICAL SOCIETY OF AMERICA was organized in 1916 "*to increase and diffuse the knowledge of optics in all its branches, pure and applied, to promote the mutual interests of investigators of optical problems, of designers, manufacturers and users of optical instruments and apparatus of all kinds and to encourage cooperation among them.*" It aims to serve the interests of all who are engaged in any branch of optics from fundamental research to the manufacture of optical goods.

MEMBERSHIP

Regular Members: "Any person who has contributed materially to the advancement of optics is eligible for regular membership."

Associate Members: "Any person who is interested in optics is eligible for associate membership."

Corporate Members: "Any corporation desirous of encouraging the work of the Society is eligible for corporation membership."

Patrons: The payment, within any one year, of $1000 or more toward the expenses of the Society by any corporation or individual entitles such corporation or individual to the rank of patron.

The Society cordially invites to membership all who are interested in any branch of optics, either in research, in instruction, in optical or illuminating engineering, in the manufacture and distribution of optical goods of all kinds or in physiological and medical optics.

ANNUAL DUES

Regular members, $8.50; Associate members, $6.00; Corporate members, $50.00; Patrons, $1000.00. These dues include subscription to the Society's official journal, the *Journal of the Optical Society of America.*

CHANGES OF ADDRESS

All changes of address of members of the Optical Society of America should be communicated to the Secretary, Professor Arthur C. Hardy, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Journal of the
OPTICAL SOCIETY
of AMERICA

VOLUME 33, NUMBER 4 APRIL, 1943

Spectrochemical Light Source Errors and Their Compensation*

H. H. GROSSMAN,† R. A. SAWYER, AND H. B. VINCENT
Randall Laboratory of Physics, University of Michigan, Ann Arbor, Michigan

MODERN spectrochemical analysis, especially of metals, now attains, for a wide range of base and alloying metals, a precision for considerable ranges of composition which is at least as good as that of chemical analysis. Such precision is not attained by all techniques or equipment. In fact, it requires a careful study of the various steps of the process, an analysis of the errors involved, and improvements where indicated.

After the errors in a particular spectrochemical procedure have been segregated and evaluated, it is possible to determine their principal sources and to test practices or variations intended to improve the method. This paper outlines one method of determining the magnitude of the various random errors of analysis. The results show that, as is true in most well-balanced procedures, the light source error is the controlling error. It is possible, then, to study the effectiveness of various methods of decreasing the source uncertainties or of compensating for them; one proposed compensation procedure is analyzed.

EXPERIMENTAL ARRANGEMENTS

The light source used in the investigation was the interrupted or controlled spark which has been described elsewhere.[1] A condenser of 0.009-microfarad capacity, charged by a transformer to 33,000 volts, is discharged by a synchronous rotary spark gap through a small inductance, resistance and the sample gap in which the $\frac{1}{8}$-inch diameter pins are mounted with a $\frac{5}{32}$-inch gap in spring clamps.

The spectrograph was a Bausch and Lomb Littrow-type quartz spectrograph used in the region 3225A to 2450A. A 40μ-slit width was used, with no condensing lens. As will be explained later, a Hilger Littrow type quartz instrument was also used in the calibrating exposures to record variations in light source intensity. Eastman Spectrum Analysis No. 1 plates were used in the work. They were developed for $2\frac{1}{2}$ minutes in a solution of three parts of Eastman D8 stock solution and five parts of water, hardened in twenty percent chrome alum solution, and fixed in acid hypo.

The microphotometer used in the plate measurements was the one previously described by Vincent and Sawyer.[2] This instrument has a wide-aperture optical system, and gives a 50-cm light-to-dark deflection with a galvanometer of two-seconds period and a photometered area of 35μ×4 mm.

* Presented in part at the Second Midwest Conference on Spectroscopy, at the University of Chicago, March 29, 1941.

† Now at Harrison Radiator Company, Lockport, New York.

[1] H. B. Vincent and R. A. Sawyer, J. App. Phys. **8**, 163 (1937).

[2] H. B. Vincent and R. A. Sawyer, J. Opt. Soc. Am. **27**, 193 (1937).

BOSTON UNIVERSITY
COLLEGE OF LIBERAL ARTS
LIBRARY

PLATE CALIBRATION

A preliminary investigation was made of methods of plate calibration to determine their applicability to the light source, plate, and photometer used. Under ideal conditions the light source and photometer should not affect the calibration. However reflections in the spectrograph or in the microphotometer may influence the light distribution on the plate or the

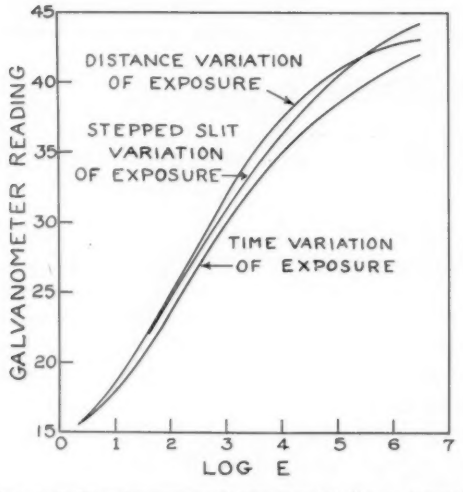


FIG. 1. Calibration curves of Eastman SA No. 1. Emulsion obtained by different techniques.

light entering the microphotometer so as to give false readings. Under these conditions it is necessary to find and use a calibration technique which gives self-consistent calibrations with the equipment used and which employs a light source and exposure time comparable to those under investigation.

The method of testing the calibration procedures was to record two sets of calibration marks on the same plate by the same method but using two light sources of different intensities.[3] The second intensity was obtained by inserting directly in front of the slit a filter made by evaporating a thin antimony film on a quartz plate. Such filters have been shown[4] to be nearly neutral over wide spectral ranges. If the calibration technique is correct two calibration curves must be obtained, when the two sets of data, taken with and without the filter, are plotted against the same exposure values, the first of which is displaced from the second at each point, on a plot of log exposure *vs.* galvanometer reading or density, by the abscissa distance of the logarithm of the ratio of the intensities of the two light sources. This quantity need not be known in advance. It is sufficient if a value can be found which translates all points of one curve onto the other within the accuracy of observation.

For the experimental conditions used in the present work, Fig. 1 shows the calibration curves obtained on Eastman SA No. 1 plates by three different techniques. In the time and in the distance-varied exposure, the experimental spark source described above was used with iron electrodes. The source was kept at a fixed distance from the slit in the first case while the exposure time was varied; in the second case a constant exposure time was used while the distance from source to slit was varied and the inverse square law of intensity variation was assumed to be valid for the small spark used. For the stepped-slit method, a source of continuous radiation—an incandescent lamp—was used and the spectrograph slit replaced by a stepped-slit, as described by Duffendack.[5]

It is clear, from the widely varying shapes of the three curves, that only one, at most, can be self-consistent for the spectral lines to be measured. When the self-consistency test was applied to them, only the inverse square method proved to give correct results. Figure 2 shows the results of this test. The data were corrected for fluctuation in the intensity of the light source by readings on spectra taken simultaneously with the Hilger spectrograph placed at a fixed distance from the source. In Fig. 2, the squares represent the uncorrected, and the triangles, the corrected data without filter, while the circles represent the data taken with the filter, corrected for intensity variation and displaced by the fixed amount which gave the best fit on the curve determined by the triangles. It is clear that the fit is as good as the experimental accuracy, and this method was accordingly adopted for the investigation.

[3] G. R. Harrison, J. Opt. Soc. Am. **18**, 492 (1929).
[4] G. O. Langstroth and D. R. McRae, Proceedings of the 5th Summer Conference, p. 105.
[5] O. S. Duffendack, J. Opt. Soc. Am. **23**, 101 (1933).

ANALYSIS OF ERRORS

In this work, studies were made of the analysis of silicon in cast iron samples containing about 1.3 percent silicon. The analytical lines used were the iron lines, 3077.2A, 3075.7A, 2880.8A, 2793.9A, and 2788.1A, and the silicon line, 2881.6A. It was found that one emulsion calibration curve satisfactorily represented the first two of these lines, and a second curve the remaining four. The plate calibration curves were obtained for each plate by measurements on several selected iron lines whose relative intensities had been determined from inverse square method exposures. The iron lines used for each curve were in a small region for which it was determined that the contrast was so constant that one calibration curve was adequate.

The silicon analysis was made with the help of a measurement of the relative intensities of the silicon line, 2881.6A, and the iron line, 2880.8A. The galvanometer measurements on these two spectral lines were used to determine the difference of the logarithms of their intensities by use of the plate calibration curve. The silicon content was then read off an analytical curve previously drawn from measurements on samples of known silicon content, and showing a straight line relationship between percent silicon and the logarithm of the intensity ratio of these two lines.

Inspection of the results of twenty-three determinations on the same plate for samples from the same lot showed an indicated silicon content varying between 1.25 percent and 1.40 percent. Part of this variation is due to sample inhomogeneity; mainly, however, it is due to other errors inherent in the analysis method. These errors are of two kinds; systematic and accidental.[6] The systematic errors arise from such causes as incorrectly analyzed standard samples, faulty calibration curves, plate background, stray light, zero drift, or sensitivity changes in the microphotometer. Accidental errors can arise from light source fluctuations, variations in emulsion thickness and sensitivity and in processing, plate grain, fluctuations in microphotometer light source, and vibrations of the galvanometer, as well as from sample inhomogeneity.

[6] R. A. Sawyer and H. B. Vincent, J. Opt. Soc. Am. **31**, 47 (1941).

In the work under consideration, numerous tests led to the conclusion that the systematic errors were small; accidental errors were the important consideration. They may be determined if it can be assumed that their causes are numerous enough and truly random so that they follow a Gaussian distribution.[7] It is convenient for analysis and further investigation to classify the random errors in spectrochemical analysis into four groups: (1) Errors in microphotometer measurements, (2) photographic emulsion errors, (3) light source errors, and (4) errors arising from sample inhomogeneity. The standard deviations[8] arising from these causes will be designated as σ_M, σ_E, σ_S, and σ_H, respectively, and the total deviation will then be $\sigma=(\sigma_M{}^2+\sigma_E{}^2+\sigma_S{}^2+\sigma_H{}^2)^{\frac{1}{2}}$.

In the experiments to determine each of these σ's, the average $\log \text{Int} \dfrac{\text{Si } 2881.6}{\text{Fe } 2880.8}$ was found and

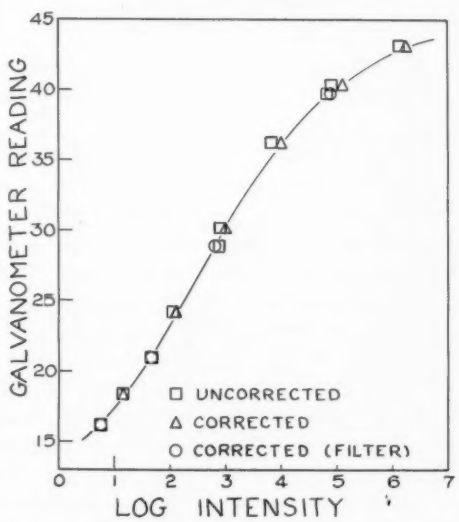


FIG. 2. Verification of self-consistency of inverse-square method of calibration.

from it the corresponding σ. This σ of $\log I$ ratio was converted into σ of percent silicon by use of the analytical curve and σ in absolute percent silicon was then reduced to σ of percent silicon

[7] See for demonstration of Gaussian distribution in a similar case, H. Kaiser, Zeits. f. tech. Physik **17**, 227 (1936).

[8] The standard deviation is $\sigma=[\Sigma d^2/(n-1)]^{\frac{1}{2}}$, where Σd^2 is the sum of the squares of the deviation from the mean of the individual results and n is the number of observations.

per unit concentration of silicon, i.e., of percent "error" in determining silicon at about one percent silicon content in cast iron, and this final σ is the one given in each case.

The standard deviation σ_M for the microphotometer was directly determined by repeated measurements of the log I ratio of the same two silicon and iron lines in one spectrum. One hundred and eight measurements yielded a value of 0.4 percent for σ_M.

To determine σ_E, the emulsion error, measurements were made of the log I ratio at each end of spectral lines made with a 10-mm slit length. Each log I ratio then involves one error due to the emulsion and one due to the microphotometer. The differences of the corresponding pairs of log I ratios should be a constant except for two emulsion and two microphotometer errors, and give for the standard deviation of the differences, $\sigma^2=2\sigma_E^2+2\sigma_M^2$. Readings on sixty-five line pairs gave $\sigma=1.0$ percent. Then $(1.0)^2=2\sigma_E^2+2(0.4)^2$, or $\sigma_E=0.6$ percent. This result is for a plate distance of 0.2 mm, which is the distance between Si 2881.6 and Fe 2880.8.

Readings of the log I ratio were then made on seventy-two spectra recorded on three plates from samples from a steel bar, rolled from a large ingot and believed to be uniform in silicon distribution. The mean deviation was calculated from the deviations from the average of each plate, and was found to be 2.2 percent. Assuming homogeneity of the sample, $(2.2)^2=\sigma_S^2+\sigma_M^2+\sigma_E^2=\sigma_S^2+(0.4)^2+(0.6)^2$ or $\sigma_S=2.1$ percent for the fluctuations of the source, including, of course, any sample inhomogeneity. Another set of sixty-seven determinations on cast iron samples recorded on five photographic plates gave an average standard deviation from the σ's for the five plates of 2.4 percent. From these data the additional error due to greater inhomogeneity of the samples, as compared with the drawn rod, is found to be $\sigma_H=1.0$ percent. The uncertainty in this figure is of course large because it is derived from the difference of the squares of two nearly equal numbers, 2.4 percent and 2.2 percent.

It should be noted that the deviations determined above are not the smallest attainable with the technique and equipment used. Recent work by H. B. Vincent and one of the authors[9] under the most favorable conditions gave the corresponding errors:

$$\sigma_M=0.18 \text{ percent}, \quad \sigma_E=0.28 \text{ percent},$$
$$\sigma_S=0.46 \text{ percent},$$

and

$$\sigma_{\text{Total}}=0.66 \text{ percent}.$$

If studies are to be made of light source fluctuations and their causes, it is clear that the source errors must be the predominant errors in the analysis. Somewhat larger errors, especially for the source fluctuations, were desired in the present work and were obtained by less critical adjustment of the operating conditions.

SOURCE ANALYSIS

Observations of interrupted spark discharges by various investigators[10] show that, in a very short time, the high voltage which is suddenly imposed on the spark gap by the closing of the synchronous interrupter gap drops to about 50 volts. From this point the discharge is a high frequency alternating current arc with the maintaining voltage practically independent of the current. The current closely follows a damped sine wave, and suddenly drops to zero after a few oscillations because the available voltage has fallen below the arc maintaining voltage. The next spark train occurs when the synchronous interrupter closes the circuit and the peak voltage of the transformer and condenser is again imposed on the spark gap.

The initial spark breakdown and the beginning of the arc are in air and result in little light emission. "Explosions" of metal vapor from the electrode surfaces then occur with the arc frequency. These luminous clouds of vapor radiate independently of the arc discharge, may continue to radiate after the arc has ceased, and emit most of the radiation of the discharge. Langstroth and McRae,[11] from relative intensity measurements on atomic tin lines and on cyanogen band lines in a condensed spark discharge between a point-plane pair of electrodes, found that the relative

[9] H. B. Vincent and R. A. Sawyer, J. Opt. Soc. Am. **11**, 686 (1942).

[10] Cf. H. Kaiser and A. Wallraff, Ann. d. Physik **34**, 297 (1939).

[11] G. O. Langstroth and D. R. McRae, Can. J. Research **16**, 17 (1938).

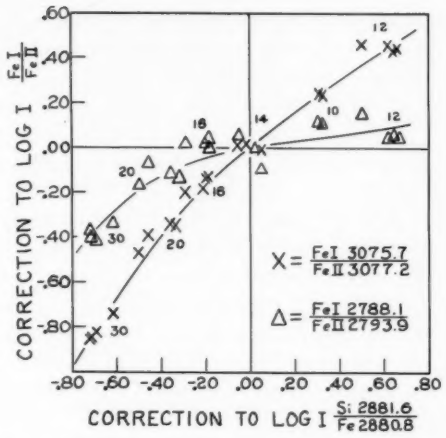


FIG. 3. Effect of number of turns of inductance on relative intensities of line pairs. One turn of inductance is approximately 3 microhenries.

intensity of the lines could be explained within the limits of the accuracy of their measurements by the assumption of a suitable average temperature of the discharge and of a Maxwell-Boltzmann distribution of the radiating atoms and molecules.

If an average temperature can be assigned to a spark discharge and if the temperature is the only parameter determining the relative intensity of the lines emitted by a spark discharge, two conclusions may be drawn. First, at a given temperature the spectral lines from a particular electrode pair should always be emitted with the same relative intensities. Second, if the temperature of a spark discharge can be determined by observation of the relative intensities of certain lines, it should be possible to correct the relative intensities of any line pair to those corresponding to another temperature.

The first of these conclusions was applied by Gerlach and Schweitzer[12] to reduce the errors due to source fluctuations. They recognized that it was not in general possible to choose an element line and a reference line which formed a truly "homologous" analytical pair—i.e., responded in the same way to changes in the excitation conditions of the source—and sought a means of assuring that the excitation conditions were reproduced each time. To this end they chose a "fixation" pair of lines of the reference element of widely different excitation properties, and of nearly equal intensities under normal conditions, and consequent widely different intensities when the excitation conditions change. They used the equality of intensities of this pair to assure that the proper temperature, and so presumably the proper excitation, had existed in the source.

This procedure, even if successful, is too slow for routine analysis, since it detects faulty conditions but does not eliminate them nor correct them. A second procedure, suggested by Levy,[13] proposed to utilize the "temperature," measured by relative line intensities, as a means of correcting the log I ratio of the analysis pair to that corresponding to the standard condition "temperature."

Levy's assumption is that the excitation in any light source is purely thermal and that the intensity ratios of any spectral line pairs, even if some reabsorption takes place, are a function of temperature only. Thus he says "we can change the intensity relations (of the spectral lines emitted by the source) only through variation of the temperature" and furthermore "the fluctuations in the light sources caused by any factor are accompanied by the change of temperature." He holds also that an effective mean temperature can be found for any exposure and then, from a previously determined relationship between the temperature and the correction to the analysis pair intensity ratio, the analysis pair intensity ratio can be corrected to that corresponding to the normal temperature. By this reduction to standard conditions, the effect of source fluctuations from any cause whatever is eliminated.

Levy proposed to find the needed relationship between temperature and correction by varying any parameter whatever of the source conditions which affects the discharge. Since he holds that fluctuations of every kind will cause intensity variations governed solely by the resulting temperature, the relation so obtained may be used for correcting any deviation found from the standard temperature regardless of its cause.

As a measure of temperature, Levy uses the intensity ratio of a "fixation pair," i.e., two lines

[12] W. Gerlach and E. Schweitzer, *Foundations and Methods of Chemical Analysis by the Emission Spectrum* (Hilger, London, 1929).

[13] S. Levy, J. App. Phys. **11**, 480 (1940).

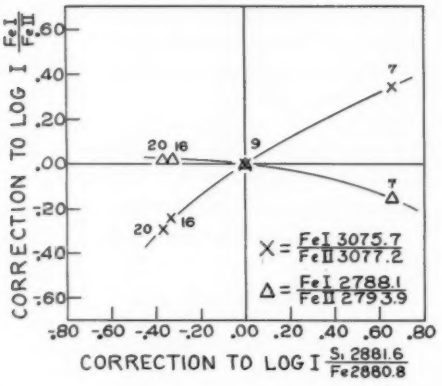


FIG. 4. Effect of number of units of capacity on relative intensities of line pairs. One unit of capacity is approximately 0.0007 microfarad.

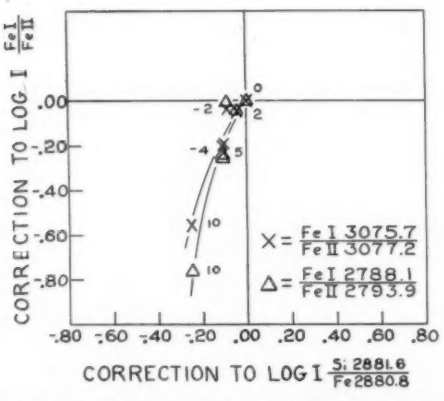


FIG. 5. Effect of change of interrupter setting, in degrees from peak voltage setting, on relative intensities of line pairs.

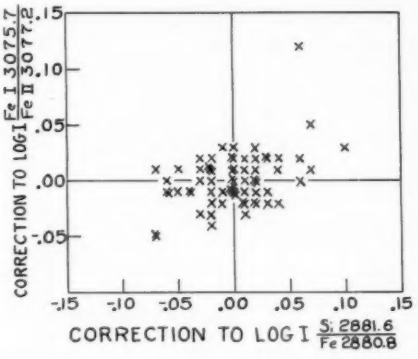


FIG. 6. Scatter diagram of change in relative line-pair intensities with normal source fluctuations for first iron pair and analysis pair.

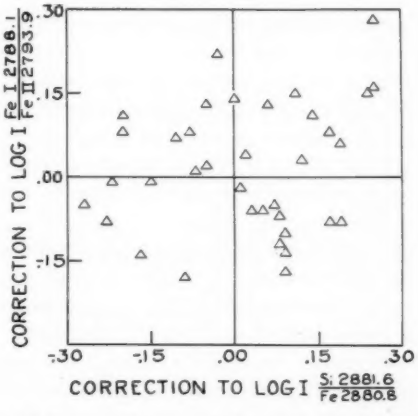


FIG. 7. Scatter diagram of change in relative line-pair intensities with normal source fluctuations for second iron pair and analysis pair.

of the reference element of widely different excitation properties, while for the analysis pair he chooses a matrix and an unknown element line which do not necessarily react in similar ways to changes in the excitation conditions. The experimental data given by Levy to support his hypothesis are not very extensive and have been made with residual errors, other than source errors, too large to permit of conclusive results.

Since the procedure, if applicable, would offer a relatively simple means of reducing source errors, a study has been made of its effectiveness for correcting the errors in spark sources. To test the theory, spectrograms were made using the same samples as electrodes but varying one of the factors affecting the operation of the light source—for example, the inductance or the capacity. The log intensity ratio was then determined for the analysis pair of lines and for a fixation pair. The corrections which must be added to these ratios to obtain the average values of the ratios found under standard conditions were then plotted against each other. In such cases, if Levy's theory is correct, a smooth curve should result and the same curve should be obtained regardless of what parameter is varied. This curve can then be used to correct the analysis pair ratios obtained in later analytical work, since, according to Levy, all such variations are due only to temperature changes.

For the tests made, the interrupted condensed spark used in the earlier part of this work was employed. For each parameter variation two fixation pairs were used: First, the iron arc line, 3075.7A, and the iron spark line, 3077.2A, and second, the iron arc line, 2788.1A, and the iron spark line, 2793.9A. Figures 3, 4, and 5 show the correction to the intensity ratio of the analysis pair for the variations of inductance, capacity, and interrupter setting, respectively, plotted against the change in the intensity of each "fixation" pair. Each point on the figures is the average of results from measurements on four spectrograms.

It will be seen that there is no general agreement among the plots for the different parameters. Except for the case of interrupter setting, the two "fixation" pairs do not give similar curves for any parameter and while the pair 3075.7–3077.2 shows a similar trend in each case, the absolute values are quite different. Variations of gap length, damping resistance, air blast pressure on the gap, electrode tip angle, and transformer primary current resulted in little or no systematic effect.

It is evident that the various parameters, while affecting relative line intensities, do not affect them in the same way. Furthermore, it is clear that if temperature is the only important factor affecting the relative intensities of lines, a plot for a series of spectrograms taken under standard conditions, of the correction to the analysis pair intensity ratio against that of fixation pair, should determine a curve which can be used for reducing any observation to the value under standard conditions. Figures 6 and 7 show such plots for the two fixation pairs. There is clearly no grouping around a curve in either case. It appears that the scattering of results with the interrupted condensed spark is due to more complicated phenomena than merely the variation of temperature of the discharge.

It seems probable that, in the case of the interrupted condensed spark, any effects due to temperature fluctuations are masked by other non-temperature-linked fluctuations of equal or greater magnitude. It was thought that the temperature effect might be more apparent in a light source with larger normal variations. The source chosen was a simple condensed spark without an interrupter but with an air blast across the spark gap. The essential distinction between the two types of spark is that, while in the interrupted spark only one sharply damped spark train occurs in each half wave of voltage, in the simple spark several spark trains of variable length and initial voltage may occur. About ten spark trains per half wave were observed with an oscillating mirror in the present case.

With this source the standard deviation for repeat determinations was 12 percent as contrasted to 2.4 percent for the interrupted spark.

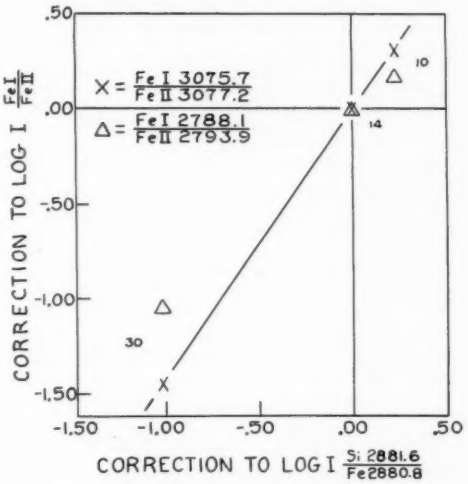


FIG. 8. Effect of number of turns of inductance on relative intensities of line pairs, second spark source.

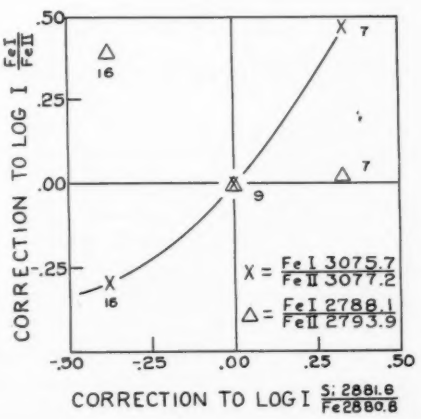


FIG. 9. Effect of number of units of capacity on relative intensities of line pairs, second spark source.

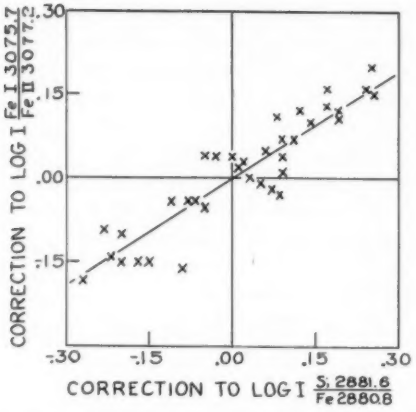


FIG. 10. Scatter diagram of change in relative line-pair intensities with normal source fluctuations for first iron pair and analysis pair, second spark source.

As before, sets of observations were made varying the different parameters. Figures 8 and 9 show plots of correction for the variation of inductance and capacity, using the same fixation pairs as in the corresponding plots of Figs. 3 and 4 for the interrupted spark. Each point in Figs. 8 and 9 is the average from measurements on seven spectrograms. It will be seen that for the pair 3075.7–3077.2, but not for the pair 2788.1–2793.9, the points show a similar trend, which is indicated by the solid line. The variation of gap length gave a similar trend for both pairs but the variation of damping resistance, transformer primary current, and strength of air blast led to effects that were small and, in general, unsystematic.

For this source, then, as for the first one tried, the variation of the possible source parameters does not lead, at least for the fixation pairs chosen, to consistent correction curves. However, when "scatter diagrams," similar to those of Figs. 6 and 7 were made, showing the correction to the analysis pair intensity plotted against the correction to the fixation pair intensity, more encouraging results were obtained.

The results are shown in Figs. 10 and 11. The results in Fig. 11 for the fixation pair 2788.1–2793.9 show no significant trend, but those in Fig. 10 for the pair 3075.7–3077.2 show a definite trend leading to the solid line which is the least square solution for the best fit. Using this line to correct the readings of Fig. 10, the standard deviation of these results was reduced from 12 percent to 4 percent, while for forty repeat observations on other plates, the deviation was reduced to 3.5 percent.

DISCUSSION OF RESULTS

It is clear from the results above that the effective mean temperature of the discharge is not the sole controlling factor in the relationship between the intensity ratios of the analysis pair and the fixation pair. For in that case the variation of different discharge parameters could not lead, as they do, to different correction curves of analysis-pair intensities against fixation-pair intensities. Further, the failure of different fixation pairs to give the same relationship is unquestionably to be attributed to the operation of at least one other factor than temperature.

In spite of the dependence of the line intensity ratios upon the operation of other factors than temperature, a simple correlation of the analysis and fixation pair ratios was found to be useful in reducing the errors in analytical determinations with the simple condensed spark, when a suitable fixation pair was used, although with the pairs investigated no such improvement was found possible with the more accurate interrupted spark. The reduction of error, obtained with the 3075.7–3077.2 fixation pair, from 12 percent to about 4 percent indicates that for this fixation pair, though not for 2788.1–2793.9, a considerable part of the fluctuations of intensity arises from causes which, if not due to tempera-

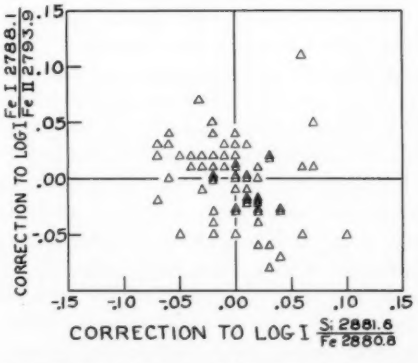


FIG. 11. Scatter diagram of change in relative line-pair intensities with normal source fluctuations for second iron pair and analysis pair, second spark source.

ture changes, at least affect the intensities of the analysis pair in the same systematic manner.

It is apparent that an effective way to seek a correlation between an analysis pair and a fixation pair is not by the variation of any one parameter, but rather by examination of the scatter diagram, such as those in Figs. 6, 7, 10, and 11, obtained under normal operation. It is necessary, too, to try several such possible fixation pairs to make sure that a satisfactory combination has been discovered.

Consideration of arc and spark behavior makes it seem probable that there are not one, but two, main causes of variation which affect the relative intensities of lines: temperature variation and vapor pressure variation. Temperature variations affect the relative numbers of atoms in the different spectral energy states, and, hence, the intensity (before any reabsorption), according to the law, $I = NP\epsilon^{-E/KT}$, where N is the number of atoms per unit volume, P is the transition probability, E is the energy difference between the initial and final states, K is the Boltzmann constant, and T is the temperature. The variation of vapor pressure affects the intensity by affecting both the number of atoms per unit volume and the amount of reabsorption of light within the luminous volume.

Temperature changes and pressure changes will not in general affect the relative intensities of different line pairs in the same way. These changes are largely independent of one another and so a correction to the apparent temperature of an earlier exposure will not generally reproduce the line intensity relations of that spectrum. Also, since the intensity ratios of various line pairs respond differently to the two effects, it will be possible by trial and error to select the pair which behaves most like the analysis pair. It will be impossible to find pairs with identical response to temperature variation since it would be necessary that corresponding lines of the pairs have the same initial and final states, and the response to vapor pressure of the two pairs can hardly be the same since one of the lines is a line of the element to be analyzed for, which certainly has a different vapor pressure-temperature relationship than the matrix element.

CONCLUSIONS

The results show that there is a partial correlation between the intensity ratio of the analysis pair in quantitative spectroscopy and the intensity ratio of the fixation pair of matrix lines, chosen to have as widely different excitation conditions as possible. The results do not, however, bear out the contention of Levy that any and all changes in source conditions produce only a change in the temperature of the source, the effect of which may be determined by arbitrary variation of any parameter and the correlation then used to correct any fluctuation resulting in practice.

It appears that if for reasons of economy or lack of equipment it is necessary to use a source involving large fluctuations, the results may be improved by the technique described in this work, which is advanced as a more effective and practical correction procedure than that proposed by Levy. In this procedure a correlation curve of fixation-pair ratio correction *versus* analysis-pair ratio correction is determined by observations taken during the normal operation of the source and used to correct later results. However, with the best modern spectrochemical sources the fluctuations can be reduced to a point below the effectiveness of this procedure.

The Spectral Characteristics of Optical Wedges

MONROE H. SWEET
Physics Division, Research Laboratories, Agfa Ansco, Binghamton, New York
(Received January 9, 1943)

OUTLINE

I. Introduction
  A. Purpose
  B. Limitations Imposed by Available Equipment
II. Method of Investigation
III. Interpretation of Results
IV. Wedges for Intensity Scale Sensitometers
  A. Photographic Wedges
  B. Carbon Wedges and Photographic Wedges Compared
V. Summary

I. INTRODUCTION

IN a previous paper[1] it was noted that the relationship between contact printing density (C.P.D.) and other types of density was approximately the same for two wedges "*E*" and "*G*" but different for wedge "*F*." All three wedges were made from common photographic materials. After contemplating these results, it became necessary to assume that, although photographic wedges are ordinarily considered neutral absorbers throughout the visual region, wedge "*F*" differs from wedges "*E*" and "*G*" as to spectral transmission.

Therefore, it seemed pertinent to the general density problem to verify experimentally the findings indicated from the previous measurements. An additional object was to demonstrate that simple densitometers can be constructed which will indicate with satisfactory precision the contact printing density (as defined in the preceding paper) of specimens having different spectral transmission characteristics.

Since this laboratory did not have easy access to an objective spectrophotometer at the time of the investigation, it was expedient to devise an apparatus which would allow measurements of the color transmission of the samples to be made easily and rapidly. While objection may be raised to the extremely abridged type of measurements adopted, it is contended that this procedure is justified in consideration of the general knowledge of the optical characteristics of the materials treated.

II. METHOD OF INVESTIGATION

To measure the spectral density characteristics of the specimens, an abridged spectrophotometer (or color densitometer) was constructed. This consisted of an Ansco Model 11 photoelectric densitometer[2] provided with a more intense light source and means for retaining gelatin color

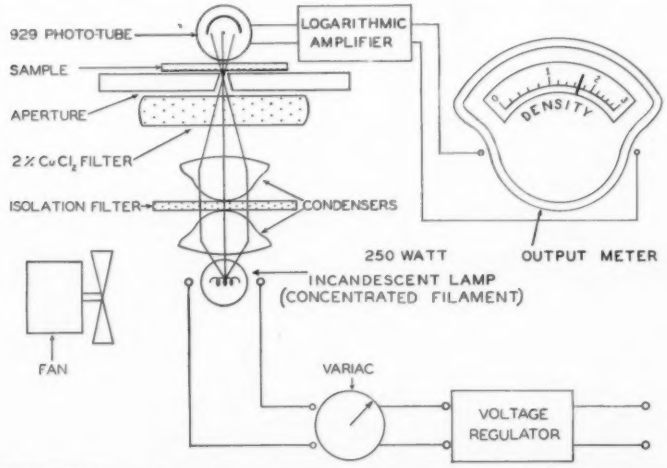


FIG. 1. Arrangement used for investigating the color density of different materials. (In the lower part of the cut the box labeled voltage regulator should read instead voltage stabilizer.)

[1] M. H. Sweet, J. Opt. Soc. Am. **33**, 143 (1943).

[2] M. H. Sweet, J. Soc. Mot. Pic. Eng. **38**, 148 (1942).

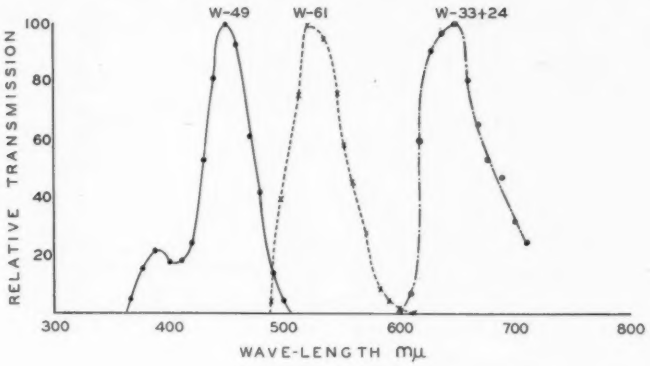


FIG. 2. Transmission curves for isolation filters used in abridged spectrophotometer (adjusted for tungsten radiation at 2750°K through 1 cm of 1.25 percent $CuCl_2$).

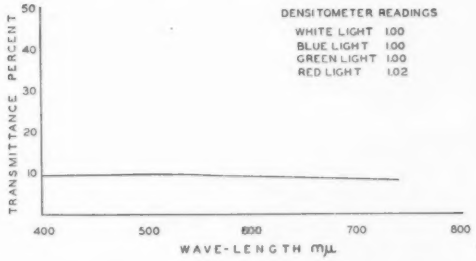


FIG. 3. Spectrophotometric curve obtained with a Hardy Automatic Recording Spectrophotometer from a normal photographic silver deposit.

filters (see Fig. 1). The instrument was also adapted to accommodate an optical cell 1 cm thick containing a 1.25 percent solution of $CuCl_2$ in order to absorb the infra-red radiation. The cell was used while making all measurements referred to in this paper. Blue densities were measured by interposing a Wratten No. 49 filter; a Wratten No. 61 filter was used for the green; and a combination of Wratten No. 33 and Wratten No. 24 was used in measuring the red densities. In Fig. 2, the spectral transmission of these filters is plotted against wave-length for tungsten radiation of color temperature 2750°K and with allowance for the absorption of the

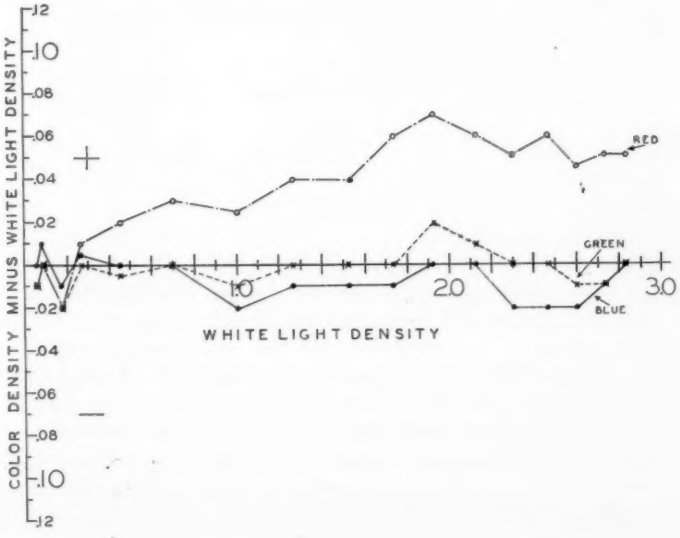


FIG. 4. Color density curves for wedge "*E*."

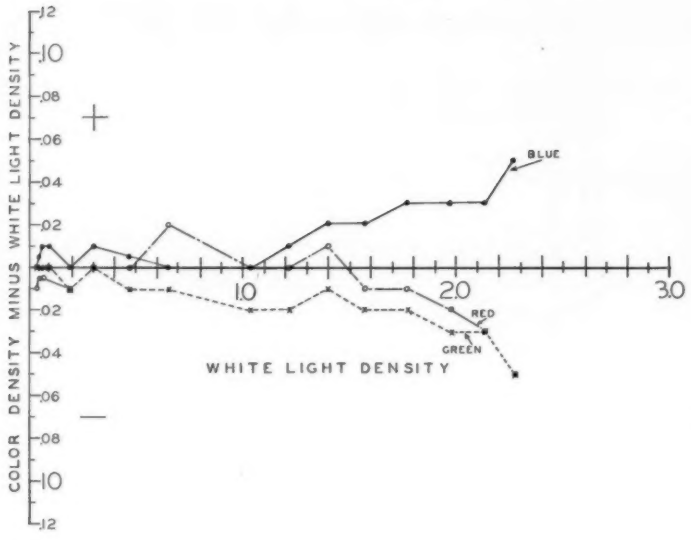


FIG. 5. Wedge "*F*" color density curves.

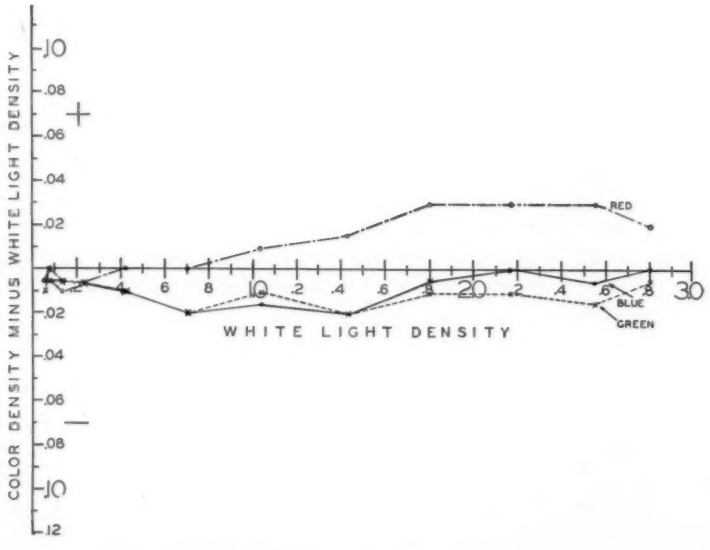


FIG. 6. Wedge "*G*" color density curves.

$CuCl_2$ solution. The curves showing the transmission of each filter have been adjusted so that the peak of each curve represents 100 percent transmission.

The spectral energy response curve illustrated in Fig. 15 of a previous article[1] for the 929 phototube was prepared from data published by the tube manufacturer.[3] Although the curve indicates zero sensitivity at wave-lengths greater than 620 mμ, the tube has a definite, if considerably reduced, sensitivity to radiation of longer wave-lengths, since it was found possible in practice to obtain full scale deflection of the output meter of the densitometer with the flux transmitted by the red filter combination, simply by increasing the voltage applied to the light source. The voltage modulation which served to control the light intensity (for zero adjustment of the

[3] *Phototubes*, RCA Manufacturing Company, Camden, New Jersey, 1940.

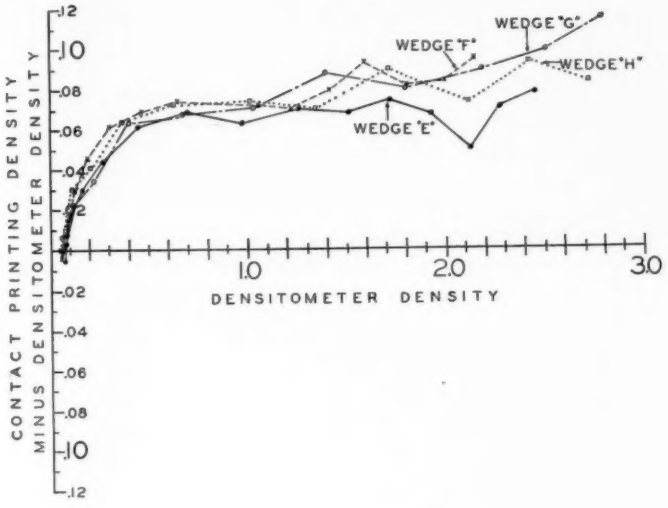


FIG. 7. C.P.D. correction curves for Ansco Model 11 No. 104 densitometer equipped with a Wratten No. 49 filter.

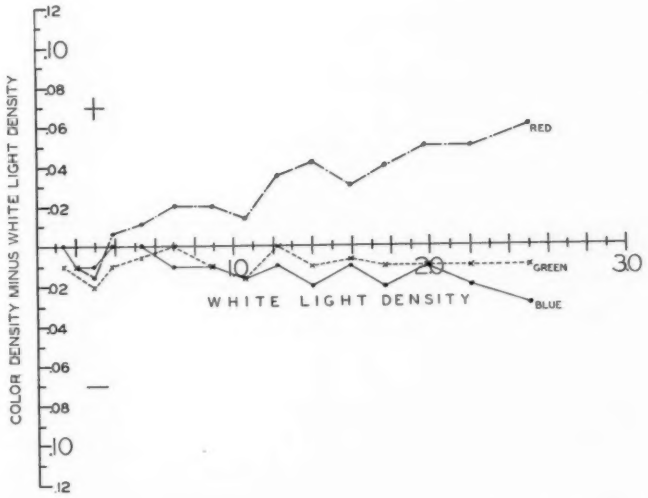


FIG. 8. Color density curves for a cine negative emulsion (Agfa Ansco Supreme) normal development.

instrument when each of the three filter combinations were used) caused differences in the color temperature of the source. However, the filter transmissions are sufficiently narrow (and practically mutually exclusive) that even wide differences in the color temperature will not appreciably affect the validity of readings through the three filters.

The reliable over-all performance and calibration of this instrument was verified by measurement of colored specimens from which complete spectrophotometric curves had been prepared. Figure 3 is a reproduction of the spectrophotometric curve obtained with a Hardy Automatic Recording Spectrophotometer. In this case, the specimen was an ordinary photographic silver deposit. The color density readings obtained for the specimen by using the present system are listed in the upper right-hand corner of this figure. The agreement is considered satisfactory. An additional verification is to be found by comparing similar data pertaining to the case of the carbon wedge discussed later.

To evaluate the neutrality of a given step-

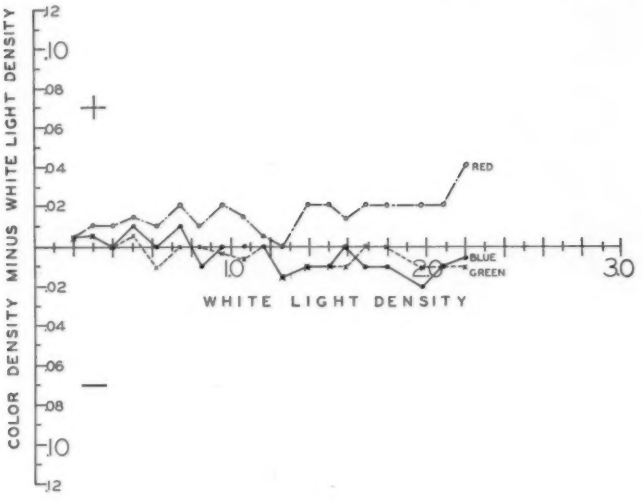


FIG. 9. Color density curves for Agfa Ansco Isopan emulsion, normal development.

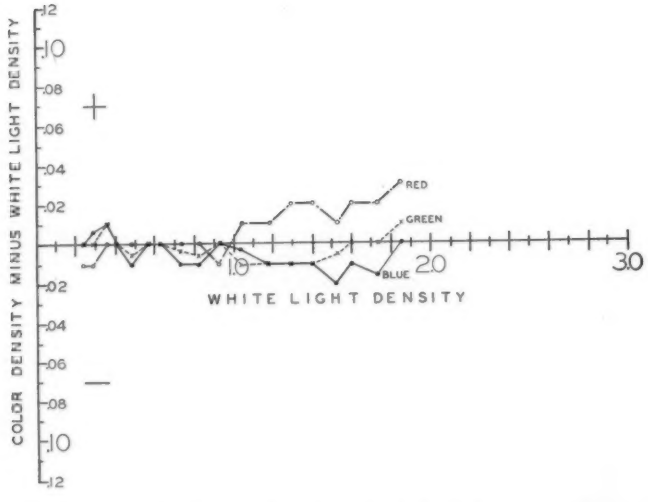


FIG. 10. Super Plenachrome emulsion, normal development.

wedge, our standard procedure involved the following readings for each specimen:

A. No color filter (white light)
B. Wratten No. 49 (blue)
C. Wratten No. 61 (green)
D. Wratten No. 33+No. 24 (red).

III. INTERPRETATION OF RESULTS

Figures 4, 5, and 6 show the differences between color density and white light density, as a function of white light density for wedges "*E*," "*F*," and "*G*." The corresponding data are given in tables *E*, *F*, and *G*, columns 7, 8, 9, and 10 in a previous article.[1] Wedges "*E*" and "*G*" exhibit similar blue and green transmission characteristics but have a higher red density, the relative value of which increases as the total density increases. Unlike "*E*" and "*G*," Wedge "*F*" is characterized by a blue density definitely greater than the red density, although the red density is sensibly greater than the green.

When these data are associated with the results of the "black and white" density measurements enumerated in the preceding article and the spectral attributes of the various optical systems are considered, the reasons for the

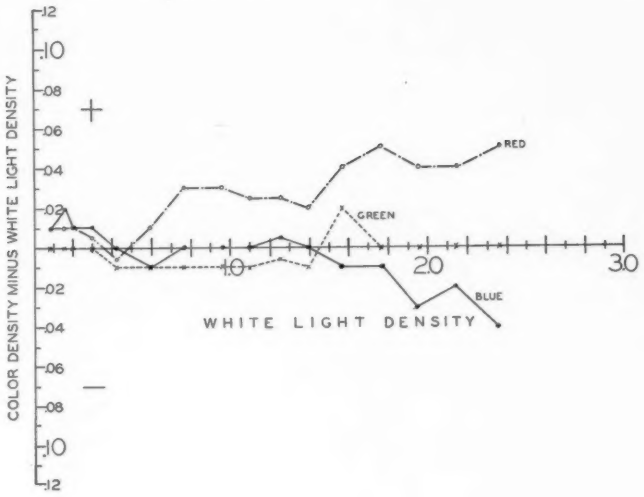


FIG. 11. Color density curves for Ultra Speed emulsion, normal development.

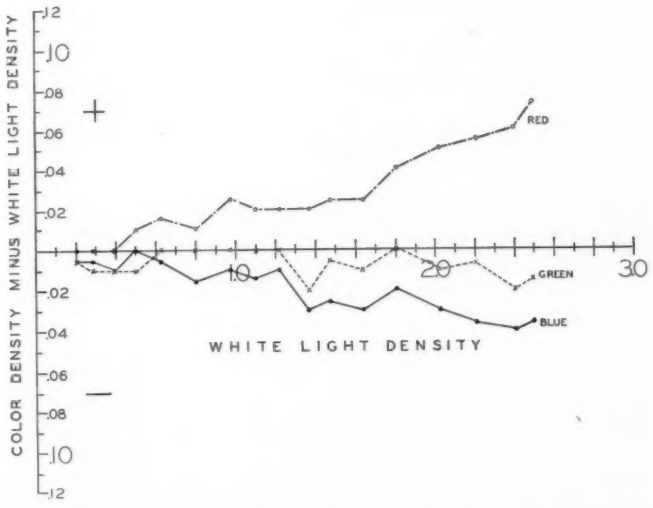


FIG. 12. Triple *S* Ortho emulsion, normal development.

general form of the comparison density curves become apparent. The higher relative sensitivity of the photographic print material to blue and violet radiation, in the case of Wedge "*F*," resulted in contact printing densities greater than the density values determined with the Martens and E.R.P.I. (normal filter) photometers, and by the experimental inverse square law photoelectric method. The similarity in spectral response of the E.R.P.I. photo-tube "printing" filter combination[4] and that of Brovira photographic paper accounts for the fact that the resulting correction curve assumes approximately the same form for all three wedges.

It is of interest to note that C.P.D. measurements made with the use of Brovira paper as the sensitive material are in good agreement with those made with the use of Positive motion picture film. The designers of the E.R.P.I. densitometer intended to provide an instrument with a spectral sensitivity duplicating that of positive motion picture film in the "printing density" adaption of the densitometer.[4] Apparently, densitometers may be readily constructed

[4] J. G. Frayne, J. Soc. Mot. Pic. Eng. **36**, 622 (1941).

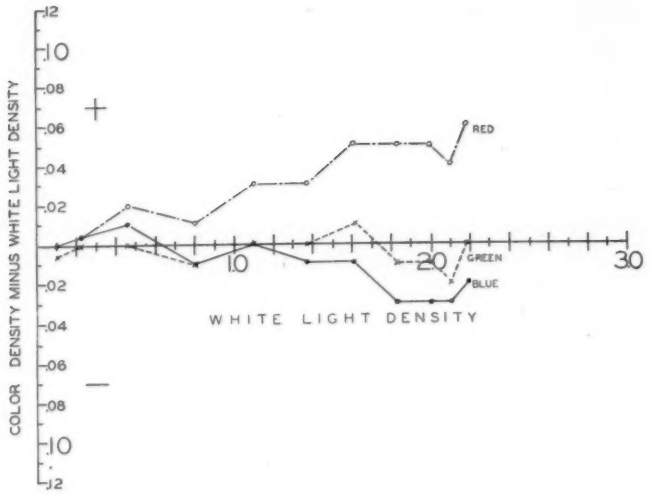


FIG. 13. Single coated x-ray emulsion coated on glass plate, normal development.

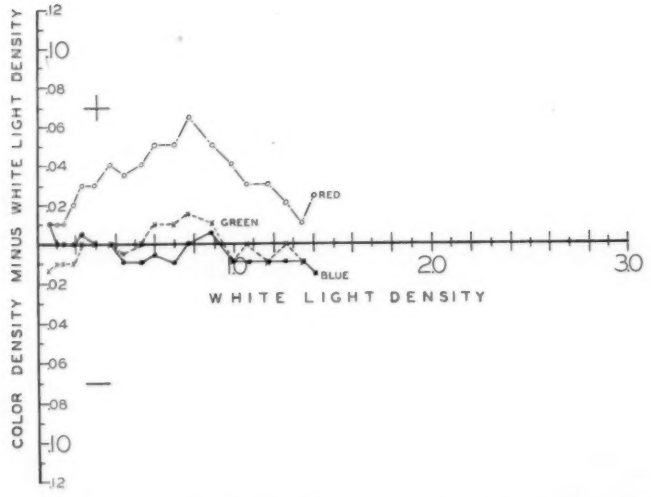


FIG. 14. Color density curves for Agfa Ansco Commercial film developed in a metol-hydroquinone developer (A-47) for three minutes.

(or existing photoelectric densitometers modified) to read C.P.D. directly for most specimens.

Curves relating C.P.D. to readings obtained with an Ansco densitometer equipped with a Wratten No. 49 filter for several different types of wedges are shown in Fig. 7. The order of agreement among the plots is within experimental error (except for the last three points of Wedge "*E*").

IV. WEDGES FOR INTENSITY SCALE SENSITOMETERS

As a result of renewed interest in intensity scale sensitometry, efforts have recently been directed toward the manufacture of wedges with satisfactory optical properties. The two general types of wedges currently of greatest interest are those moulded from colloidal carbon dispersed in a suitable vehicle and those prepared photographically.

A. Photographic Wedges

The transmission characteristics of various photographic layers (silver deposits formed by exposure and development of many different kinds of emulsions) have been studied with the aid of our abridged spectrophotometer. Silver layers formed in a single type of emulsion, but

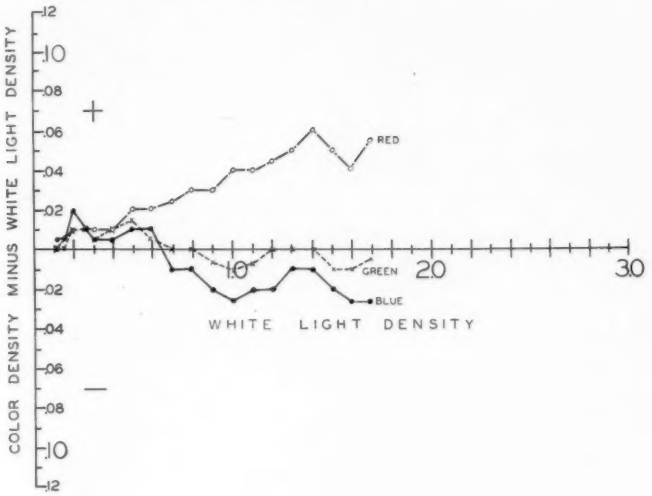


FIG. 15. Commercial film developed for four minutes in A-47.

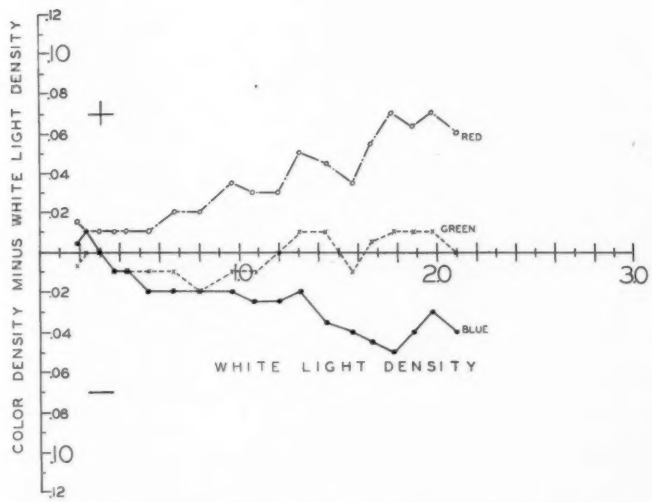


FIG. 16. Commercial film developed for six minutes in A-47.

developed under different conditions, were also studied.

In view of the markedly different relative spectral transmission of Wedge "*F*" and that of Wedges "*E*" and "*G*," it appeared that a sample exhibiting substantially neutral absorption might be found. Figures 8 through 14 represent the relative color densities of seven different types of emulsions developed in normal developers. In every case, the red density is characteristically higher than the blue and green densities.

Figures 14 through 17 demonstrate the effect of variation in time of development for Commercial film. Commercial film has a single coated emulsion of moderately fine grain and rather high inherent contrast. The red-green-blue density relationship is not appreciably affected by variation of developing time. Figures 17 through 20 illustrate the color density relationships for a single type of emulsion, processed in different developers. Here again, the color-density relationship is not influenced appreciably.

Because Wedge "*F*" was made from Process emulsion and gave a color density relationship unlike that of the other two wedges, Process film was used for a series of wedge exposures, and was developed for different times. Figures 21 through 23 are color density curves for develop-

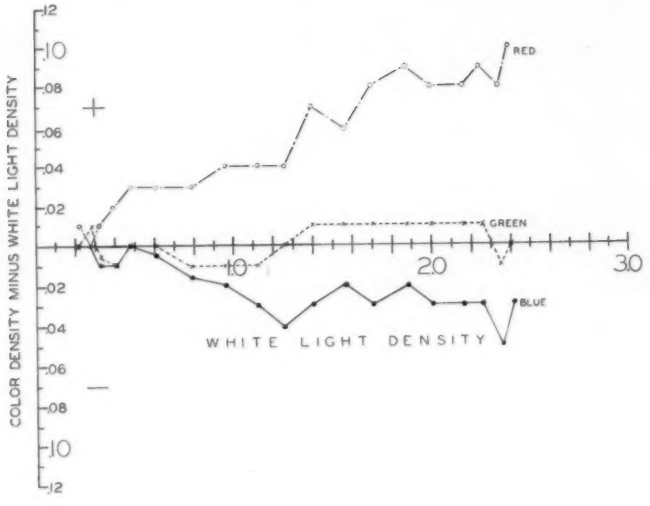


FIG. 17. Commercial film developed for ten minutes in A-47.

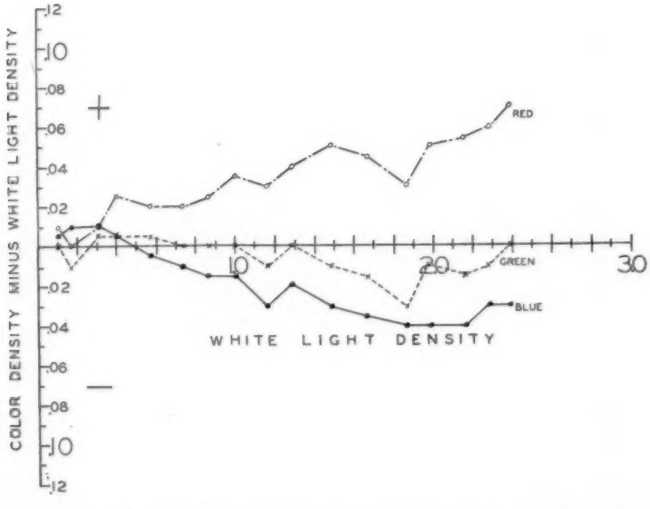


FIG. 18. Commercial film developed for a normal length of time in a Metaborate developer, Agfa 48-M.

ing times of 2, 4, and 6 minutes, respectively, in A-47 (a metol-hydroquinone developer). The example of Process film which has been underdeveloped is a conspicuous exception to the general case of color density distribution. In all other studies, thus far (excluding dye images), a higher red density relationship is the rule.

B. Carbon Wedges and Photographic Wedges Compared

In the light of these data, it appeared worth while to examine photographic and carbon wedges sold commercially for use in intensity scale sensitometers. One photographic wedge was found to have the color densities represented in Fig. 24. The corresponding values for a cast colloidal carbon wedge are given in Fig. 25. As anticipated, the photographic wedge showed a typical spectral density distribution but the carbon wedge was notably different in respect to color characteristics, having a *blue density considerably greater* than the red and green densities.

From this evidence, it was expected that the effective C.P.D. of the *photographic* wedge, as used in sensitometers, would be the same for all color blind and orthochromatic materials, but would be slightly different for panchromatic emulsions. Color blind and orthochromatic ma-

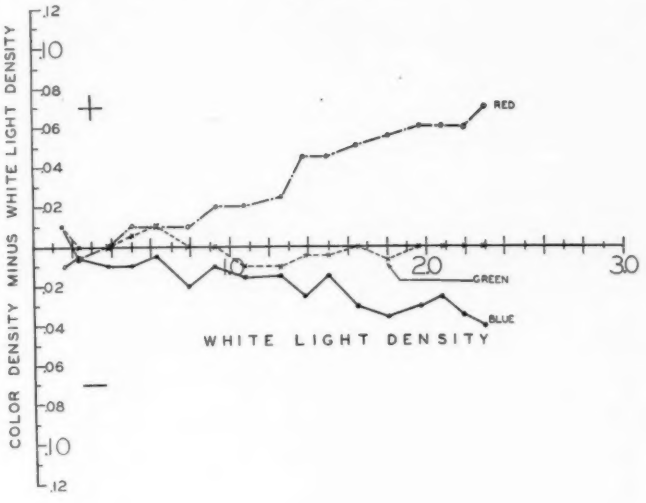


FIG. 19. Commercial film developed in a special M-H developer of ratio $3\frac{1}{2}$: 1.5, for a normal length of time.

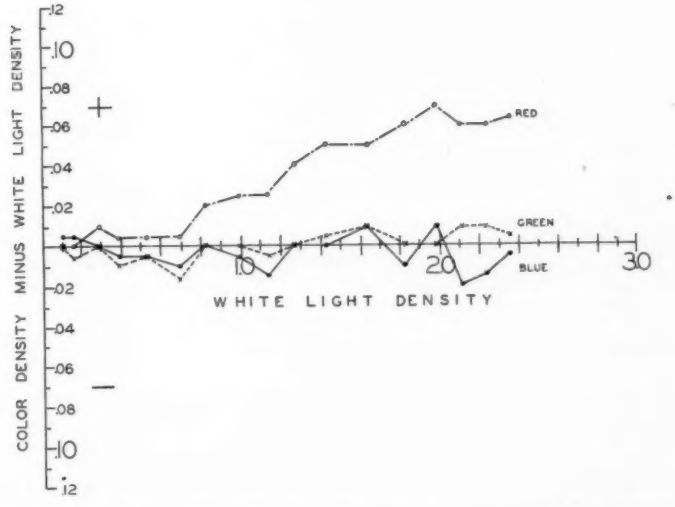


FIG. 20. Commercial film developed in Eastman D.K. 50, another M-H developer—normal developing time.

terials, being insensitive to red, would not be affected by the higher red densities of the photographic wedge.

The *carbon* wedge could be expected to exhibit different effective photographic densities for color blind, orthochromatic, and panchromatic sensitive materials, because apparently there is an abrupt change in color density of the wedge between the blue-violet and the green region of the spectrum (see Fig. 26).*

* A complete spectrophotometric curve supplied by the manufacturer was later made available to the writer. It is reproduced in Fig. 26.

Considering the purposes for which optical wedges are employed, it is especially appropriate that their densities be measured by the contact printing method. However, instead of using a silver bromide emulsion alone, the print material should ideally be altered to include emulsions representative of those for which the sensitometer will be used.

Both the photographic and the carbon wedge were measured by the C.P.D. method, using Process film (non-color sensitized), Standard roll film (low orthochromatic) and Superpan Portrait cut film (high panchromatic sensitivity). Wedge

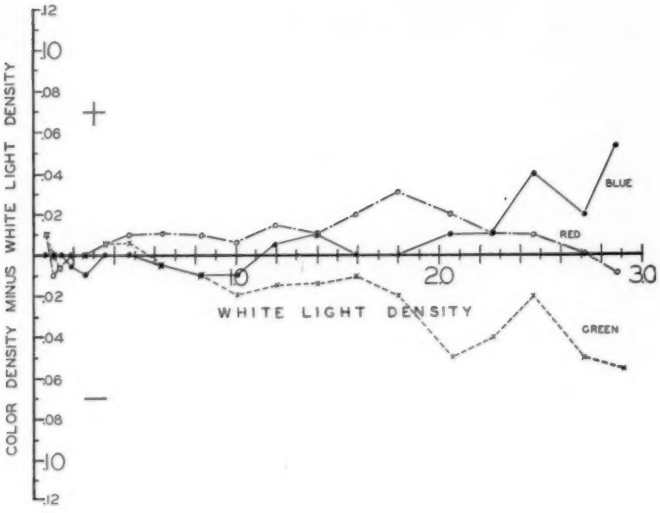


FIG. 21. Agfa Ansco Process emulsion developed for three minutes in A-47.

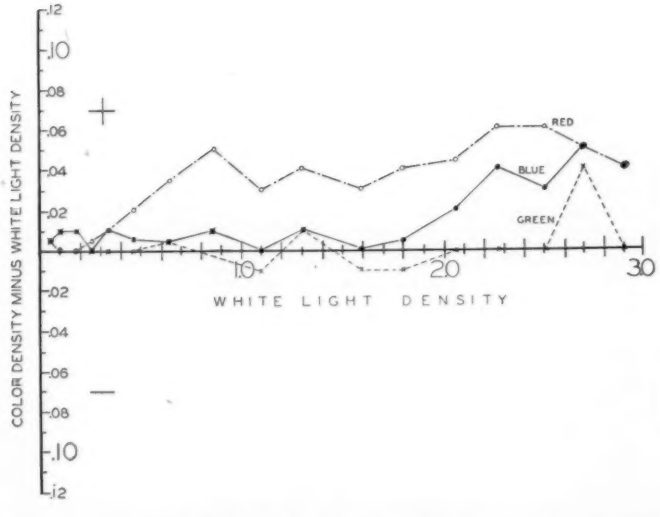


FIG. 22. Process emulsion developed for four minutes in A-47.

spectrograms of these films are shown in Fig. 27. The results are tabulated in Tables I and II and are plotted graphically in Figs. 28 and 29. Although the photographic wedge was badly abraded, a circumstance that made measurement difficult, the results bear out the assumption that all classes of emulsion would show about the same contact printing density values for this wedge.

C.P.D. data obtained with the carbon wedge are also in accord with previous expectations. The effective contact printing density for Super-pan Portrait film was 0.10 lower at a density level of 3.0 than the contact printing density determined for process film. Therefore, sensitometric exposures based on any specific set of density values for the carbon wedge cannot be correct for all classes of sensitized material. On the other hand, a single calibration of the photographic wedge will evidently be sufficient for use with materials having color sensitivity in any of the three classes represented.

In addition to the density measurements already discussed, both of these wedges have been

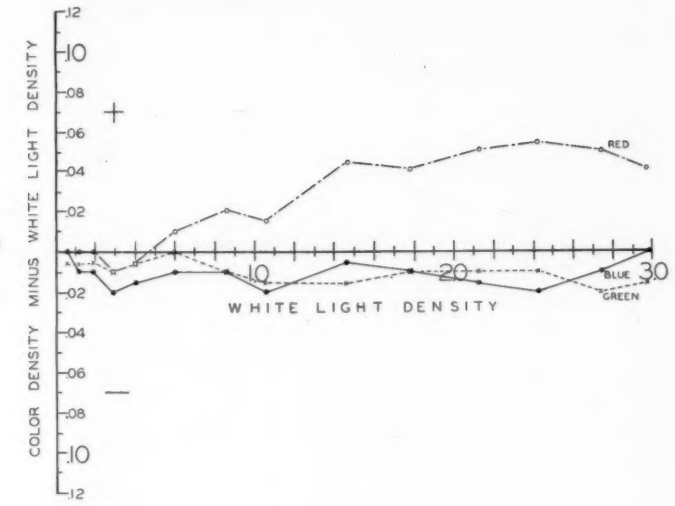


FIG. 23. Process emulsion developed in A-47 for six minutes.

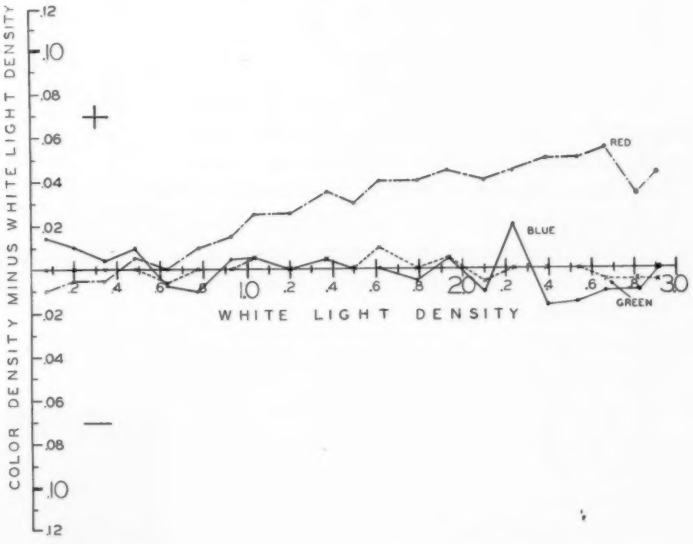


FIG. 24. Color density plot of a commercially available photographic wedge manufactured for use as a modulation in intensity scale sensitomerers.

measured by the photo-cell-inverse square law technique,* and the results are included in Tables I and II. The photographic wedge was also measured to determine the C.P.D. values, using Brovira paper as the print material. Column 5 of Table I lists the results of this work. In general, the latter values are the same as those obtained by using Process film (compare wedge spectrograms).

Column 2 of Table II lists the "Diffuse density" values of the carbon wedge, as determined by the manufacturer. While there is no mention of the exact method of measurement on the manufacturers' calibration data sheet,** the values assigned invariably lie between the C.P.D. measurements obtained by using Superpan film and those obtained by using Process film.

* For details of the method see reference 1.

** It is stated, however, "that a Callier quotient of 1.47 was deliberately chosen in order to obtain the closest possible approach to spectral neutrality."

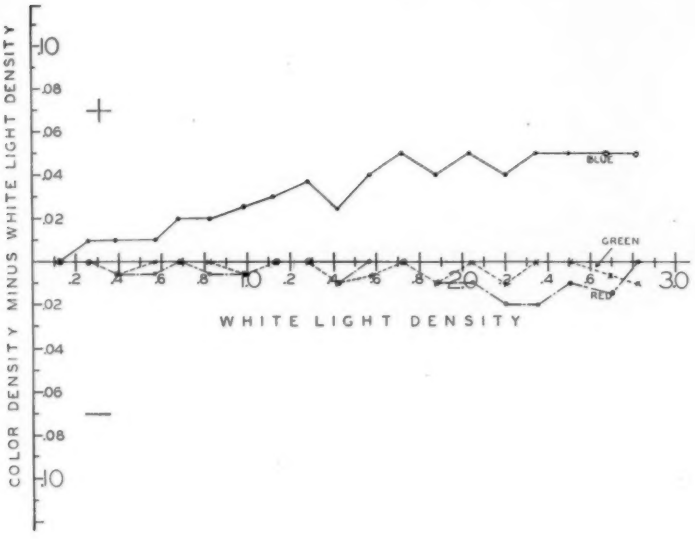


FIG. 25. Color density curves for a commercially available colloidal carbon wedge.

V. SUMMARY

An investigation of the color density of optical transparency wedges has shown that specimens prepared from a number of photographic emulsions under different conditions exhibit approximately the same color density relationship. Such wedges are characterized by a higher red density than blue or green. An exception to this general case is that of a slow speed bromide emulsion, underdeveloped.

It has been demonstrated that a simple photoelectric densitometer which reads contact printing density directly can readily be constructed. The instrument gives satisfactory accuracy for specimens having a variety of spectral transmission characteristics.

A comparison has been made between the spectral transmission properties of photographic and carbon wedges manufactured commercially for use in intensity scale sensitometers. Contact printing density measurements of these wedges were made under conditions duplicating sensitometric practice. The results confirm the superior performance predicted for the photographic wedge on the basis of earlier abridged spectrophotometric measurements.

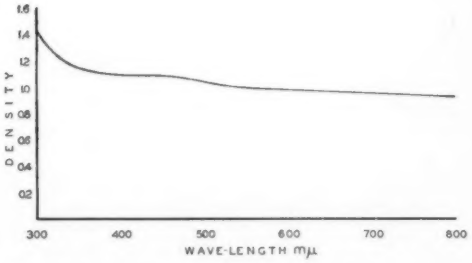


FIG. 26. Spectrophotometer curve of carbon specimen (manufacturer's data).

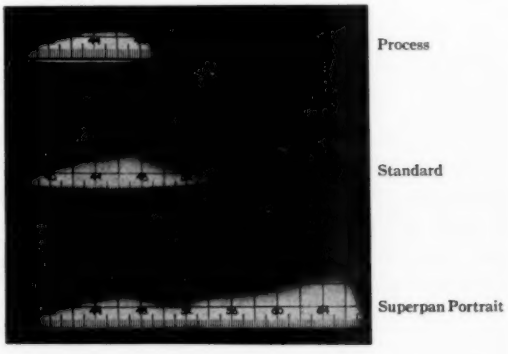


FIG. 27. Wedge spectrograms of the three types of sensitized materials used for C.P.D. measurements of wedges. (Wave-length values are millimicrons $\times 10^{-1}$.)

TABLE I. Density values for intensity scale sensitometer wedge (photographic).

(1)	(2)	(3)	(4)	(5)	(6)	Model 11 No. 104 Densitometer +1 cm of 1.25% $CuCl_2$			
	Color blind	Ortho-chromatic	Pan-chromatic			(7)	(8)	(9)	(10)
Step	C.P.D. Process	C.P.D. Standard	C.P.D. Superpan	C.P.D. Brovira	$\frac{1}{\square}$ P.E.	No filter	Blue (W 47)	Green (W 61)	Red (W 33) (W 24)
1	0.108	0.121	0.085	0.091	0.0586	0.08	0.095	0.08	0.07
2	.253	.235	.218	.251	.2300	.20	.21	.20	.195
3	.404	.434	.370	.407	.3744	.325	.33	.325	.32
4	.542	.556	.508	.547	.5264	.465	.475	.465	.47
5	.698	.714	.690	.703	.6862	.62	.615	.615	.62
6	.835	.841	.807	.853	.8384	.76	.75	.76	.77
7	1.000	1.003	1.010	1.000	.9974	.91	.915	.91	.925
8	1.162	1.154	1.144	1.154	1.1606	1.06	1.065	1.065	1.085
9	1.308	1.312	1.314	1.321	1.3258	1.21	1.21	1.21	1.235
10	1.470	1.487	1.462	1.468	1.4868	1.35	1.355	1.355	1.385
11	1.609	1.604	1.627	1.620	1.6426	1.505	1.505	1.505	1.535
12	1.777	1.770	1.799	1.756	1.7698	1.625	1.625	1.635	1.665
13	1.935	1.924	1.889	1.935	1.9490	1.795	1.79	1.795	1.835
14	2.167	2.128	2.118	2.154	2.1120	1.94	1.945	1.945	1.985
15	2.209	2.254	2.184	2.257	2.2722	2.10	2.09	2.095	2.14
16	2.373	2.385	2.357	2.383	2.4272	2.23	2.25	2.23	2.275
17	2.553	2.530	2.525	2.538	2.5812	2.385	2.37	2.385	2.435
18	2.697	2.671	2.640	2.673	2.7384	2.525	2.51	2.525	2.575
19	2.875	2.853	2.819	2.839	2.8898	2.68	2.67	2.675	2.735
20	2.982	2.979	2.922	2.985		2.81	2.80	2.805	2.845
21						2.91	2.91	2.905	2.955

TABLE II. Density values for intensity scale sensitometer wedge (carbon).

(1)	(2)	(3)	(4)	(5)	(6)	Model 11 No. 104 Densitometer +1 cm of 1.25% $CuCl_2$				
		Color blind	Ortho-chromatic	Pan-chromatic		(7)	(8)	(9)	(10)	(11)
Step	Values supplied by wedge manufacturer	C.P.D. (Process)	C.P.D. (Standard)	C.P.D. (Superpan)	$\frac{1}{\square}$ P.E.	No filter	No filter*	Blue (W 47)*	Green (W 61)*	Red (W 23)* (W 24)
1	0.21	0.243	0.220	0.218	0.2500	0.125	0.20	0.20	0.20	0.20
2						.26	.33	.34	.33	.33
3	.52	.542	.530	.511	.5504	.395	.475	.485	.47	.47
4						.54	.62	.63	.62	.615
5	.82	.840	.825	.787	.8494	.685	.76	.78	.76	.76
6						.825	.92	.94	.92	.915
7	1.12	1.151	1.110	1.078	1.1472	.99	1.065	1.09	1.06	1.06
8						1.13	1.21	1.24	1.21	1.21
9	1.43	1.445	1.435	1.383	1.4450	1.27	1.35	1.385	1.35	1.35
10						1.42	1.51	1.535	1.50	1.50
11	1.74	1.771	1.725	1.692	1.7558	1.57	1.64	1.68	1.635	1.64
12						1.72	1.80	1.85	1.80	1.80
13	2.05	2.062	2.030	1.962	2.0626	1.875	1.96	2.00	1.95	1.95
14						2.04	2.11	2.16	2.11	2.10
15	2.36	2.370	2.365	2.293	2.3808	2.19	2.27	2.31	2.26	2.25
16						2.34	2.42	2.47	2.42	2.40
17	2.67	2.710	2.7005	2.627	2.6976	2.50	2.58	2.63	2.58	2.57
18						2.67	2.735	2.785	2 73	2.72
19	2.98	3.060	3.020	2.935	2.9656	2.82	2.86	2.91	2.85	2.86
20						2.87	2.98		2.985	2.98

* Since the densitometer could not be brought to zero for the red filter readings when the thickness of the carbon wedge mount was interposed, readings of the other color densities were made with a similar zero setting and an additional set of white light values was included to permit an intercomparison of results with the other sets of results.

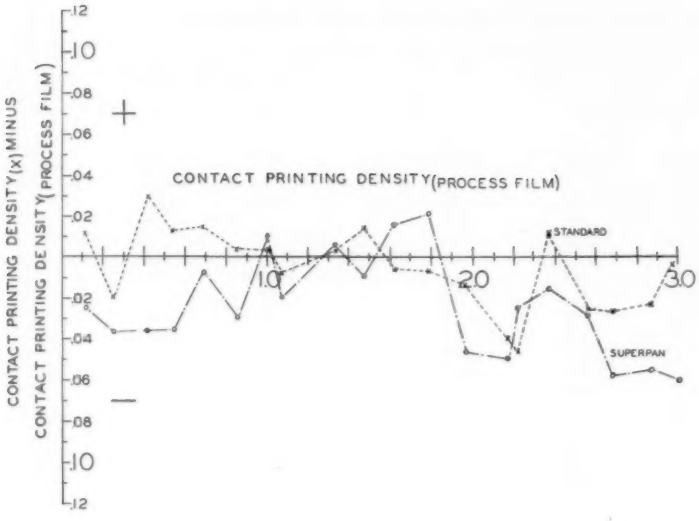


FIG. 28. Comparison of C.P.D. measurements on a photographic wedge, using three different types of sensitized print material. Axis—Process film (color blind; x------ Standard film (low orthochromatic); — - — Superpan film (high panchromatic).

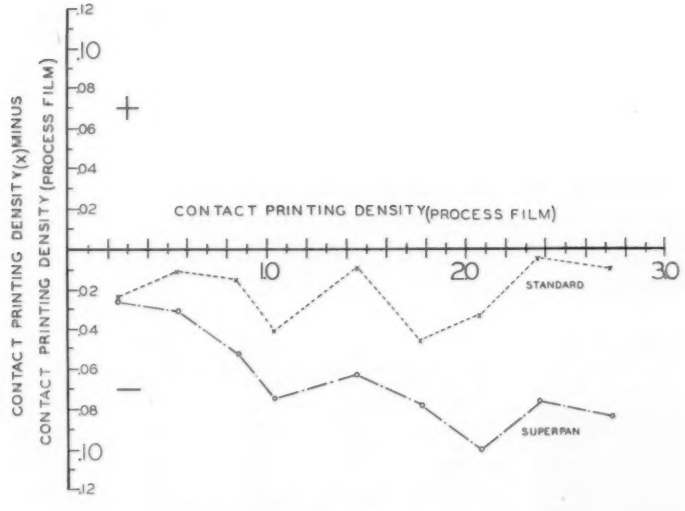


FIG. 29. Comparison of C.P.D. measurements on a colloidal carbon wedge. Axis—Process film; x------ Standard film; — - — Superpan film.

ACKNOWLEDGMENT

The writer is appreciative of the assistance of Mr. Robert Johnston, of this laboratory, for his diligent cooperation in making the numerous necessary measurements. His constructive criticism of the C.P.D. method as it developed is also appreciated. The friendly suggestions of many other members of Agfa Ansco have resulted in numerous improvements in the experimental work and in the preparation of the manuscripts.

The Ultraviolet Absorption Spectra of Protein Solutions[1]

R. NORMAN JONES, *Harvard University, Cambridge, Massachusetts, and Queen's University, Kingston, Canada*

AND

HUGH J. CREECH, *The University of Maryland, College Park, Maryland*

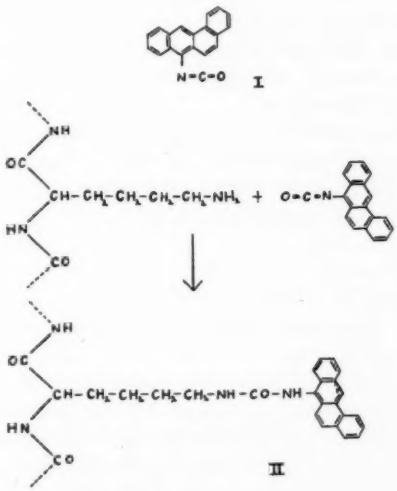
A method is described for the spectrographic analysis of conjugated proteins, formed by the interaction of serum proteins with the isocyanates of certain polynuclear aromatic hydrocarbons. The method makes possible the determination of the number of hydrocarbon groups introduced into each protein molecule, provided the hydrocarbon chromophore has maxima at wave-lengths greater than 3250A. At wave-lengths less than 3250A, where the chromophoric groups of the normal protein also absorb, the total absorption is shown not to be equivalent to the sum of the absorptions of the several chromophoric groups involved. The spectra of binary solutions of the unconjugated protein and a simple, water soluble, compound containing the hydrocarbon chromophore, exhibit deviations from the calculated summation spectra which are of a similar character to those exhibited by the conjugated proteins. It is shown that the scattering of light by the protein molecule plays no direct part in this effect. The absorption spectra of mixtures of *l*-tyrosyl-*l*-tyrosine and horse serum albumin do not exhibit abnormal behavior; the observed spectra are closely similar to those calculated from the summation of the spectra of the two solutes. Although the abnormalities in the spectra of protein solutions do not appear to be of a general character, attention is drawn to the possibility that effects of this nature may occur in other solutions containing proteins. Care must be exercised, therefore, in the application of spectrophotometry and colorimetry to the analysis of substances in the presence of proteins.

PART I. THE ABSORPTION SPECTRA OF HYDROCARBON-CARBAMIDO PROTEINS

Introduction

IN a recent series of papers[2–4] a description has been given of the preparation and properties of several conjugated proteins, formed by the reaction of serum proteins with the isocyanates of certain polynuclear aromatic hydrocarbons. 1,2-benzanthryl-10-carbamido horse serum albumin, which is prepared by the action of 1,2-benzanthryl-10-isocyanate (I) on horse serum albumin, is typical of such conjugates.

Reaction occurs between the isocyanate group and the ε-amino group of the lysine side chains of the protein, with replacement of the ε-amino group by the hydrocarbon-carbamido system (II). The coupling process may be so controlled as to vary the number of introduced hydrocarbon-carbamido groups over a wide range. A spectrophotometric method has been developed by means of which the number of hydrocarbon groups introduced into any given preparation can be determined.



The spectra of the serum albumins and globulins have absorption maxima near 2750A (Fig. 1), mainly due to the phenol and indole chromophores of the tyrosine and tryptophane side chains.[5,6]

[1] Presented, in part, at the Tenth Summer Conference on Spectroscopy and its Applications, at Massachusetts Institute of Technology, Cambridge, Massachusetts, July 20–22, 1942. Correspondence concerning this paper should be addressed to R. N. Jones at Queen's University, Kingston, Canada.

[2] H. J. Creech and R. N. Jones, J. Am. Chem. Soc. **62**, 1970 (1940).

[3] H. J. Creech and R. N. Jones, J. Am. Chem. Soc. **63**, 1661 (1941).

[4] H. J. Creech and R. N. Jones, J. Am. Chem. Soc. **63**, 1670 (1941).

[5] Dhéré, *L'absorption des rayons ultraviolets par les albuminoïdes, les proteides et leurs derivées* (Fribourg, 1909).

[6] E. R. Holiday, Biochem. J. **30**, 1795 (1936); E. R. Holiday and A. G. Ogston, Biochem. J. **32**, 1166 (1938).

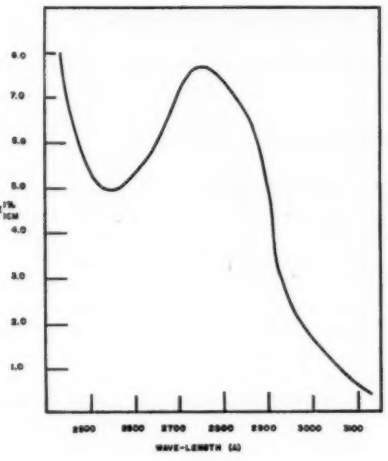
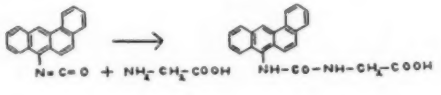


FIG. 1. Absorption spectrum of horse serum albumin.

On the long wave-length side of this maximum the intensity falls off rapidly, and at wave-lengths greater than 3250A, the absorption is negligible. The spectra of the hydrocarbon-carbamido proteins differ from the spectra of natural serum proteins; several maxima occur in the region between 3250 and 4000A, and this absorption is characteristic of the particular hydrocarbon group introduced. Apart from a small bathochromic shift, it resembles very closely the absorption of the carbamidoacetic acid derivative, which is formed by the action of the hydrocarbon isocyanate with glycine (III).



III

Ramart-Lucas,[7] Arnold and Kistiakowsky,[8] and others have shown that a chromophore contributes additively to the light absorption of a molecule when it is separated from any other chromophore in the same molecule by two or more methylene ($-CH_2-$) groups. In the conjugated proteins discussed here, four methylene groups separate the hydrocarbon-carbamido chromophore from the protein chain, so that theoretically such groups attached to the lysine side chain should absorb independently of the other chromophoric centers in the protein molecule. The experimental results confirm this *insofar as the absorption at wave-lengths greater than 3250A is concerned.*

The over-all absorption of these protein conjugates may be regarded as a summation of two components, one due to the aromatic side chain groups of the normal serum proteins, and the second to the absorption of the hydrocarbon-carbamido groups. In the discussion which follows, these are referred to as the *protein component* and *hydrocarbon component*, respectively.

The negligible absorption of the protein component at wave-lengths greater than 3250A, makes it possible to calculate the number of hydrocarbon groups combined with each protein molecule directly from measurements of the intensity of the absorption maxima in this region of the spectrum, since all the absorption can be attributed to the hydrocarbon component. The absorption curve is measured for a standard concentration of the conjugated protein solution (1 g per 100 ml) and the intensity of the maxima between 3250 and 4000A compared with the intensity of the corresponding maxima of a standard solution of the carbamido-acetic acid derivative of the same hydrocarbon-carbamido group. The algebraic treatment of this analysis has been developed elsewhere[2,3] (together with a discussion of the assumptions which are involved), and leads to the following equation:

$$C = \frac{1600\ (\log I_0/I)_{max}}{E'_{max}\ Nl},$$

where C = the number of mg of hydrocarbon-carbamido radical combined with 1 gram of protein;

$(\log I_0/I)_{max}$ = the photometric density at an absorption maximum between 3250 and 4000A in the spectrum of the conjugate;

N = the nitrogen content in mg per ml of the conjugated protein solution;

[7] P. Ramart-Lucas, "Structure des Molecules et Spectres d'Absorption. Spectres dans l'Intra-violet et Spectres dans le Visible." Grignard, *Traité de Chimie Organique*, (Masson et Cie., Paris, 1936), Vol. II, Part I.

[8] L. B. Arnold, Jr., and G. B. Kistiakowsky, J. Am. Chem. Soc. **54**, 1713 (1932).

l = the length of the absorption cell in cm;

E'_{max} = a constant for a particular absorption maximum, involving the intensity of the corresponding maximum in the spectrum of the hydrocarbon-carbamidoacetic acid derivative, the molecular weight of the hydrocarbon-carbamidoacetic acid derivative, and the molecular weight of the hydrocarbon radical.

This method of analysis has been applied with success to several conjugates in which the hydrocarbon components have conveniently located maxima (see Table I). The simpler aromatic chromophores, including the phenyl, α-naphthyl, and β-naphthyl groups do not give carbamidoacetic acid derivatives or conjugates with absorption maxima in this region of the spectrum, and cannot be analysed in this manner. A study has been made of the absorption spectra of some conjugates at shorter wave-lengths, where the contribution of the protein component to the total absorption can no longer be neglected, with the object of developing a method suitable for the analysis of conjugates containing these simpler aromatic systems.

Spectra of Conjugates in the Further Ultraviolet (3250-2400A)

If the contributions to the total light absorption of the protein and hydrocarbon components were independent, the analytical problem would be closely parallel to the determination of a solution containing two absorbing solutes, the spectrum of each of which is known. The concentration of each solute in such a solution can be calculated directly from the absorption spectrum of the binary mixture by a method which has been developed by Vierordt[9] and further elaborated by Philpot.[10] Mixtures of tyrosine and tryptophane have been analysed in this manner by Holiday,[6] who obtained results which compared favorably in accuracy with those given by the orthodox methods of chemical analysis.

TABLE I. Polynuclear aromatic hydrocarbon groups which have been estimated spectrographically in conjugated proteins.

β-Anthryl	10-Methyl-1,2-benzanthryl-3-
1,2-Benzanthryl-10-	3,4,-Benzpyrenyl-5-
1,2-Benzanthryl-3-	1,2,5,6-Dibenzanthryl-9-

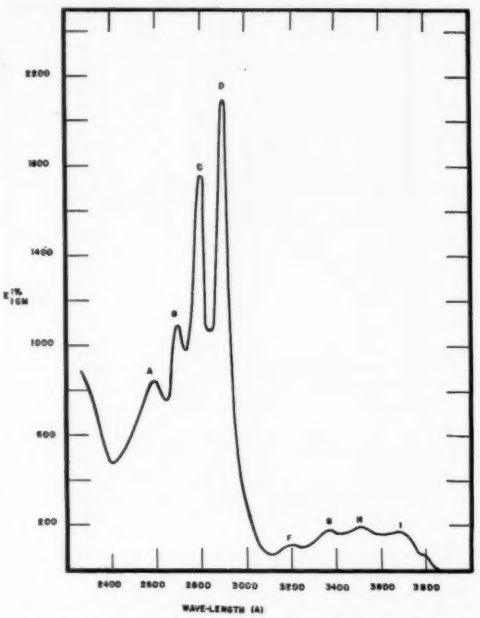


FIG. 2. Absorption spectrum of 1,2-benzanthryl-10-carbamidoacetic acid.

In adapting such a method to the analysis of the absorption spectra of the conjugated proteins into protein and hydrocarbon components, certain difficulties were anticipated as the coupling process produces a slight but significant shift of the absorption maxima toward the red. On analysis of the curves, deviations of a much more serious character were observed which could not be attributed to this cause and which would appear to make impracticable any extension of the analytical technique along these lines.

The absorption spectrum of a solution of 1,2-benzanthryl-10-carbamido acetic acid (III) in a sodium borate/boric acid buffer at pH 8.0 is shown in Fig. 2. The maxima are designated by a system of lettering established in an earlier paper

[9] F. Twyman and C. B. Allsopp, *The Practice of Absorption Spectrophotometry* (Adam Hilger Ltd., London, 1934), p. 41.

[10] Private communication to E. R. Holiday (see reference 6).

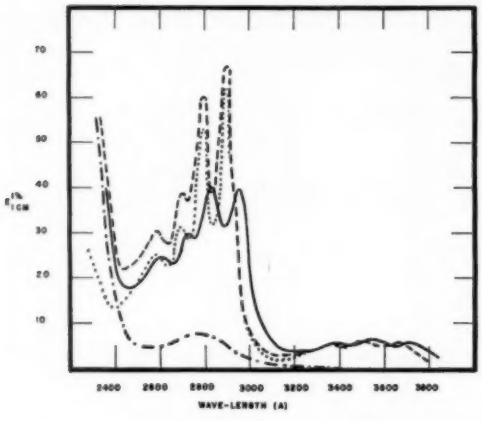


FIG. 3. Absorption spectrum of 1,2-benzanthryl-10-carbamido horse serum albumin. (*A*) ——— Observed curve; (*B*) -·-·-·- Calculated protein component; (*C*) ····· Calculated hydrocarbon component; (*D*) – – – – – Calculated summation curve (*B*+*C*).

for 1,2-benzanthracene.[11] In Table II the intensities of the maxima ($E^{1\%}_{1\text{ cm}}$) are recorded as obtained in five separate determinations. ($E^{1\%}_{1\text{ cm}}$ is the extinction coefficient for a 1-cm path length of a solution containing 1 gram of solute per 100 ml of solution.) The spectrum of horse serum albumin in the same solvent[12] is illustrated in Fig. 1, while that of a typical preparation of 1,2-benzanthryl-10-carbamido horse serum albumin is shown in Fig. 3, curve *A*. Calculations based on the intensities of the *G*, *H*, and *I* maxima of Fig. 3, curve *A* by the methods already established,[2,3] indicate that the preparation contains 20 mg of 1,2-benzanthryl-10- radical per gram of protein.

From the data provided in Figs. 1 and 2 and Table II the protein and hydrocarbon components of Fig. 3, curve *A* can be calculated. These are curves *B* and *C* (of Fig. 3), respectively. The sum of curves *B* and *C* should be identical with the observed curve *A* if the Vierordt equation is to apply accurately. Actually the summation curve (*D* of Fig. 3) differs considerably from the experimentally observed curve (*A*). Calculations of the 1,2-benzanthryl content of the conjugate based on measurements in the neighbourhood of the *C* and *D* maxima would differ considerably from those calculated on the basis of the *G*, *H*, and *I* maxima.

Further examples to illustrate this depressed absorption in the region of the *C* and *D* maxima are given in Table III where data for the intensity of the *C*, *D*, and *H* maxima of several preparations are analyzed into the two components. In all cases the observed intensities of the *C* and *D* maxima are much below those calculated from the *G*, *H*, and *I* maxima. In the calculations included in Table III an approximate correction is made for the shift in the position of the absorption maximum on conjugation, by calculating the intensity of the protein component for the wave-length of the observed conjugate maximum. Thus, in Preparation I, the protein component for the *D* maximum is calculated for 2950A instead of for 2903A, the wave-length of the *D* maximum of 1,2-benzanthryl-10-carbamidoacetic acid.

The deviations between the observed and calculated intensities in this region of the spectrum are of such a magnitude as to make impossible the extension of this method of analysis to conjugates in which the hydrocarbon component does not contain maxima at longer wave-lengths.

PART II. THE ABSORPTION SPECTRA OF SOLUTIONS OF HORSE SERUM ALBUMIN AND 1,2-BENZANTHRYL-10-CARBAMIDOACETIC ACID

In an endeavor to obtain further information concerning the depression of the absorption maxima reported in the preceding part of this paper, some measurements have been made of the

TABLE II. Wave-lengths and intensities of the absorption maxima of 1,2-benzanthryl-10-carbamidoacetic acid.

Max.	*A*	*B*	*C*	*D*	*G*	*H*	*I*
Wave-length (A)	2590	2690	2796	2903	3359	3520	3688
Intensity ($E^{1\%}_{1\text{ cm}}$)							
Exp. 1	850	1090	1750	2070	174	198	181
Exp. 2	875	1095	1740	2005	181	210	181
Exp. 3	—	—	—	—	171	192	171
Exp. 4	820	1050	1800	2100	171	197	171
Exp. 5	—	—	1780	2100	170	210	170
Mean	848	1078	1770	2069	173	203	175

[11] R. N. Jones, J. Am. Chem. Soc. **62**, 148 (1940).

[12] The absorption curve of horse serum albumin is distinctly unsymmetrical, but no structure could be resolved in the region between 2800–2900A. A specimen of crystalline zinc insulin measured at *p*H 4.0 gave a well-marked inflection at 2830A, similar to that found by Darby for Papain in 0.01*N* HCl. [See H. H. Darby, J. Biol. Chem. **139**, 721 (1941).]

spectra of solutions of horse serum albumin and 1,2-benzanthryl-10-carbamidoacetic acid (III). This system differs from the protein conjugate discussed in Part I in that the two chromophoric groups are present in the mixture in separate molecules.

The absorption curve of one such mixture is shown in Fig. 4 (curve *A*). The mixture was made from standard solutions of horse serum albumin and 1,2-benzanthryl-10-carbamidoacetic acid; the curve for the protein component is *B* of Fig. 4, while that calculated for the mixture is curve *C*. The curve for the 1,2-benzanthryl-10-carbamidoacetic acid component is omitted from the diagram to avoid overcrowding. As in the case of the conjugated proteins, the observed absorption curve is much less intense in the neighborhood of the *C* and *D* maxima than that calculated by summation of the component curves. Several further examples of the same type are given in Table IV. These mixtures exhibit a bathochromic shift in the position of the absorption maxima, although this is less pronounced than the shift observed in the spectra of the conjugated protein. At longer wave-lengths (3250–4000A) the presence of the protein produces no effect on the intensity of the absorption of the carbamidoacetic acid compound. This is illustrated by the agreement between the observed and calculated intensity data for the *H* maximum in Table IV.

TABLE III. Observed and calculated intensities of the *C*, *D*, and *H* maxima for various preparations of 1,2-benzanthryl-10-carbamido horse serum albumin.

	Mg of hydrocarbon per gram of protein	Wave-length	Intensity*			
			Protein component	Hydrocarbon component	Total Calc.	Total Observed
			C maximum			
A	20	2835A	6.8	52.5	59.3	40.2
B	38	2845	6.8	101	107.8	82
C	36	2840	6.8	96	102.8	81.5
D	36	2850	6.8	96	102.8	84.2
E	41	2840	6.8	109	115.8	100
			D maximum			
A	20	2950	2.5	62.5	65	40.2
B	38	2955	2.5	119	121.5	92
C	36	2950	2.5	113	115.5	81.5
D	36	2960	2.5	113	115.5	84.2
E	41	2960	2.5	128	130.5	100
			H maximum			
A	20	3555	0.0	6.1	6.1	6.0
B	38	3570	0.0	11.7	11.7	11.9
C	36	3570	0.0	11.0	11.0	11.0
D	36	3565	0.0	11.0	11.0	11.0
E	41	3565	0.0	12.6	12.6	12.5

* The intensity is calculated for 1-cm path length of a solution containing 1 gram of protein in 100 ml of solution ($E^{1\%}_{1\ cm}$). See Experimental Technique, Part II of this paper.

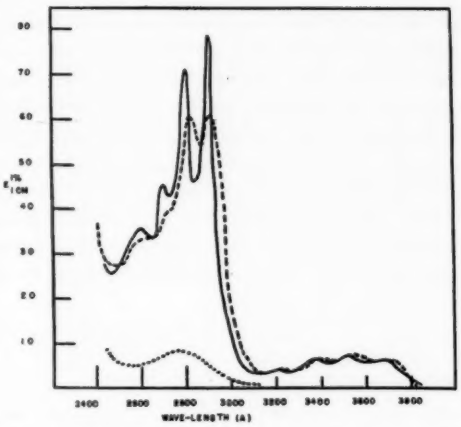


FIG. 4. Absorption spectrum of a binary solution of horse serum albumin and 1,2-benzanthryl-10-carbamidoacetic acid. (*A*) – – – – Observed curve; (*B*) ····· Calculated protein component; (*C*) ——— Calculated summation curve. (The hydrocarbon component curve is not shown.)

The abnormal absorption of these mixtures is even more difficult to interpret than that of the conjugates, and suggests that the effect must be attributed to a physical rather than a chemical origin. In any protein solution, certain optical anomalies may be anticipated due to the secondary effects of light scattered by the large molecules concerned and although these measurements were made on solutions which were optically clear on gross inspection, it seemed possible that light scattered by the protein molecules may play some part in producing the effects observed.

The experiment illustrated diagrammatically in Fig. 5 was devised to test this hypothesis and to provide further evidence of the objective nature of the effect, under conditions which exclude any assumptions in the calculation of the component curves from being contributory causes.[13]

The spectrophotometer was so arranged that light from a continuous source passed consecutively through two separate cells, *A* and *B*, two identical cells *C* and *D* being placed in the control beam of the Spekker photometer. A solution of 1,2-benzanthryl-10-carbamidoacetic acid in a buffer solution of *p*H 8.0 was placed in cell *A* and a solution of horse serum albumin in the same solvent in cell *B*; cells *C* and *D* contained the sol-

[13] This experiment was suggested by Dr. Hugh H. Darby.

vent only, and the concentrations of the solutes in cells *A* and *B* were so adjusted that the *C* and *D* absorption maxima were measured under conditions of optimum sensitivity. Curve *A* of Fig. 6 was obtained under these conditions. Cells *A* and *B* were next interchanged so that the light passed first through the protein solution and then through the solution of 1,2-benzanthryl-10-carbamidoacetic acid; the curve obtained under these conditions was identical with curve *A* (Fig. 6).

Cells *A* and *B* were next emptied, the cells cleaned and dried, the two solutions mixed and both cells filled with the mixture. The spectrum of this system (curve *B* of Fig. 6) differs considerably from that given by the two unmixed solutions; the maxima are depressed and shifted to longer wave-lengths, in agreement with the observations reported previously. Cells *A* and *B* were emptied again, cell *B* was filled with the protein solution and cell *A* with the buffer solvent. The absorption curve of the protein component (*C* of Fig. 6) of the mixture was thus determined experimentally and the hydrocarbon component was finally determined in a similar manner (curve *D*).

The curves in Fig. 6 illustrate clearly that the depression in the intensities of the absorption is only observed when the protein and hydrocarbon-carbamidoacetic acid molecules are together in intimate contact in the same solution; the sum of the experimentally determined component curves *C* and *D* (Fig. 6) fits reasonably closely to the curve observed when the light passes through the two solutions consecutively.

TABLE IV. Observed and calculated intensities of the *C*, *D*, and *H* maxima for solutions of horse serum albumin and 1,2-benzanthryl-10-carbamidoacetic acid.

	Mg of 1,2-benzanthryl-10-carbamido-acetic acid per gram of protein	Wave-length	Intensity* Calculated: Protein component	Hydro-carbon component	Total	Observed total
			C maximum			
A	71	2810	7.4	126	133.4	121
B	29	2810	7.4	52	59.4	43.8
C	35.8	2820	7.4	64	71.4	60.5
D	12	2845	7.0	21.5	28.5	24.8
			D maximum			
A	71	2910	4.5	147	151.5	133
B	29	2910	4.5	60	64.5	48.6
C	36.8	2910	4.5	74	78.5	60.5
D	12	2950	2.5	24.8	27.3	22.6
			H maximum			
A	71	3530	0.0	14.4	14.4	14.0
B	29	3530	0.0	5.9	5.9	5.6
C	35.8	3540	0.0	7.3	7.3	7.5
D	12	3540	0.0	2.4	2.4	2.1

* Calculated for a solution containing 1 g of horse serum albumin per 100 ml of solution. See Experimental Technique, Part II of this paper.

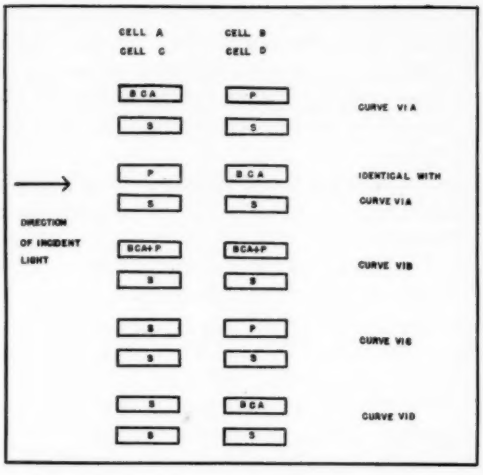


FIG. 5. Arrangement of cells in experiment illustrated in Fig. 6. (*B C A*) Solution of 1,2-benzanthryl-10-carbamidoacetic acid; (*P*) Solution of horse serum albumin; (*BCA+P*) Mixture of above solutions in equal proportions; (*S*) Solvent solution (buffer of *p*H 8.0).

These observations rule out a simple scatter effect as an explanation of the fall in intensity, and emphasize the pronounced bathochromic shift in the position of the maxima. Such a shift would normally be interpreted as evidence of chemical combination, but that explanation is excluded in this case since 1,2-benzanthryl 10-carbamidoacetic acid can be rapidly and completely separated from the mixed solution by dialysis. The observed displacement of the spectrum might be caused by adsorption of the 1,2-benzanthryl-10-carbamidoacetic acid molecules on the protein, with a resultant lowering of the activation energy of the electron levels in the aromatic chromophore. A somewhat similar effect is frequently observed during the reversible adsorption of dyestuffs on activated alumina from organic solvents, where yellow dyes often form red adsorption complexes indicating a shift of the absorption maxima of the chromophore of the dye molecule toward longer wave-lengths. Such an explanation does not take into consideration the fact that the absorption of 1,2-benzanthryl-10-carbamidoacetic acid at longer

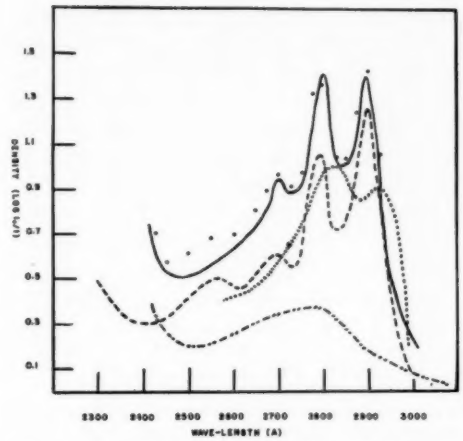


FIG. 6. Absorption spectra of solutions of horse serum albumin and 1,2-benzanthryl-10-carbamidoacetic acid. (*A*) ————; (*B*) ·····; (*C*) – · – · – · –; (*D*) – – – –. For description of curves see Fig. 5. ○ Points on the summation curve (*C*+*D*).

wave-lengths does not appear to be influenced by the protein, and the effect is only significant when the protein component is itself contributing to the total light absorption of the system.

Experimental Technique

1,2-benzanthryl-10-carbamidoacetic acid, crystalline horse serum albumin and 1,2-benzanthryl-10-carbamido horse serum albumin were specimens of material the preparation and purification of which have been described.[2-4] Solutions of 1,2-benzanthryl-10-carbamidoacetic acid were prepared by weighing the solid on a microbalance, dissolving in the buffer solution, and diluting to standard volumes. The concentration of the protein solutions were determined by micro-Kjeldahl analysis, using the figure of 16 percent for the nitrogen content of crystalline horse serum albumin.[14] All measurements were made in a sodium borate/boric acid buffer solution at *p*H 8.0, the *p*H being determined with a glass electrode.

The absorption measurements were made with a Bausch and Lomb medium quartz spectrograph, a Hilger Spekker photometer, and a hydrogen discharge tube; further details of the experimental conditions have been described elsewhere.[11]

[14] T. L. McMeekin, J. Am. Chem. Soc. **61**, 2884 (1939).

The methods of calculation of the 1,2-benzanthryl content of the conjugated proteins are discussed in the Introduction of Part I and in more detail in earlier publications.[2-4] The hydrocarbon components of the conjugate spectra were calculated as follows:

If the conjugate contain w mg of 1,2-benzanthryl- radical per gram of protein, as determined from the intensities of the *G*, *H*, and *I* maxima, a solution containing 1 g of conjugated protein in 100 ml of solution will contain w mg of benzanthryl radical, equivalent spectrographically to

$$w \cdot \frac{344}{227} \text{ mg of 1,2-benzanthryl-10-carbamidoacetic acid.}$$

If the value of $E_{1\text{ cm}}^{1\%}$ for 1,2-benzanthryl-10-carbamidoacetic acid at the wave-length λ is E_λ', the intensity of the 1,2-benzanthryl component of the conjugate (E_λ^h) will be

$$E_\lambda^h = E_\lambda' \cdot \frac{344}{227} w \cdot 10^{-3}.$$

As the calculations are all expressed in terms of a solution containing 1 g of protein conjugate per 100 ml of solution, the protein component (E_λ^p) can be taken equal to $E_{1\text{ cm}}^{1\%}$ for horse serum albumin, it being assumed that the change in molecular weight of the protein on conjugation is negligible.

The total calculated absorption (E_λ^c) is therefore given by the expression

$$\begin{aligned} E_\lambda^c &= E_\lambda^h + E_\lambda^p \\ &= \frac{344}{227} w \cdot 10^{-3} \cdot E_\lambda' + E_\lambda^p \\ &= 1.51 w E_\lambda' \cdot 10^{-3} + E_\lambda^p. \end{aligned}$$

Values of E_λ' for the maxima are given in Table II and for all values of E_λ^p and E_λ' can be interpolated from Fig. 1 and Fig. 2, respectively.

For mixtures of 1,2-benzanthryl-10-carbamidoacetic acid and horse serum albumin, the concentrations are known from the conditions under which the solutions were prepared. If the concentration of the 1,2-benzanthryl-10-carbamidoacetic acid solute be w' mg per gram of protein, the absorption intensity of a solution containing 1 g

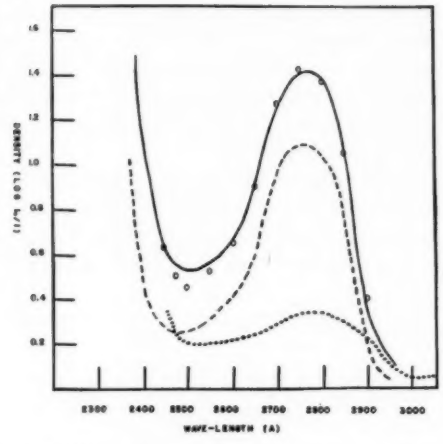


FIG. 7. Absorption spectrum of a mixture of *l*-tyrosyl-*l*-tyrosine and horse serum albumin (concentrations of 139γ and 412γ per ml, respectively). (*A*) ———— Observed curve; (*B*) – – – – – Calculated curve for the *l*-tyrosyl-*l*-tyrosine component; (*C*) ····· Calculated curve for the protein component; ○ Points on the summation curve (*B*+*C*).

of protein in 100 ml of solution, measured in a cell of 1-cm path length (E_λ^m) is given by

$$E_\lambda^m = w' \cdot E_\lambda' \cdot 10^{-3} + E_\lambda^p.$$

PART III. THE INFLUENCE OF HORSE SERUM ALBUMIN AND OF 1,2-BENZANTHRYL-10-CARBAMIDOACETIC ACID ON THE ABSORPTION SPECTRUM OF *l*-TYROSYL-*l*-TYROSINE

The anomalous absorption exhibited by mixtures of horse serum albumin and 1,2-benzanthryl-10-carbamidoacetic acid, discussed in the previous section of this paper, was not anticipated and it seemed reasonable to inquire whether similar effects might not be operating in the normal serum proteins to exert a depressing influence on the contributions of the tyrosine, tryptophane, and phenylalanine side chains to the light absorption of the protein molecule. Holiday[6] has described a method of estimating the content of tyrosine and tryptophane groups in protein molecules by a mathematical analysis of the absorption spectrum determined in strongly alkaline solution; under these conditions the absorption of the phenylalanine chromophore is negligible and the content of tyrosine and tryptophane can be calculated from the intensity of absorption at 3050 and 2800A. Holiday has obtained results by this method which agree very satisfactorily with

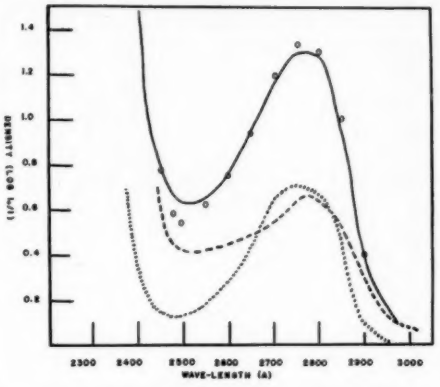


FIG. 8. Absorption spectrum of a mixture of *l*-tyrosyl-*l*-tyrosine and horse serum albumin (concentrations of 89.5γ and 832γ per ml, respectively). Curves as in Fig. 7.

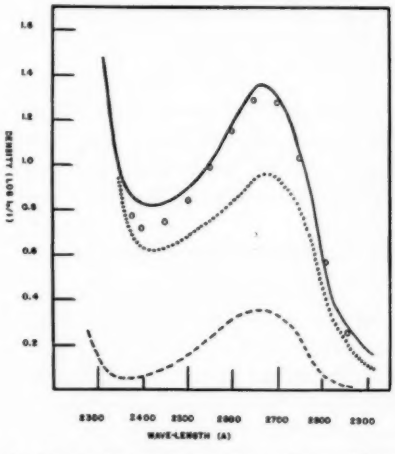


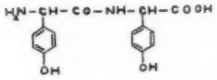
FIG. 9. Absorption spectrum of a mixture of *l*-tyrosyl-*l*-tyrosine and horse serum albumin (concentrations of 44.7γ and 1225γ per ml, respectively). Curves as in Fig. 7.

those found by the more laborious chemical methods of analysis. It is assumed by Holiday that the intensity of absorption of the tyrosine and tryptophane chromophores is the same when the groups are attached to proteins as when they are present in the low molecular weight amino acids. Lavin, Loring, and Stanley[15] have observed that the spectra of virus proteins possess an absorption maximum near 2650A which varies in intensity with the nucleic acid content of the virus. These workers have not claimed that the

[15] G. I. Lavin, H. S. Loring, and W. M. Stanley, J. Biol. Chem. **130**, 259 (1939).

nucleic acid content of the virus can be accurately calculated by analysis of the absorption curve, but an extension of their work along these lines may be possible.

If the depression of the absorption maxima discussed in Parts I and II of this paper were found to be a general one (not specific to 1,2-benzanthryl-10-carbamidoacetic acid and related compounds), serious errors may be met with in the extension of analytical work of this character. It therefore seemed advisable to make further studies of the effect, and we were fortunate in being able to obtain a sample of the synthetic dipeptide, *l*-tyrosyl-*l*-tyrosine (IV).[16] Some spectrographic measurements were made on solutions containing mixtures of *l*-tyrosyl-*l*-tyrosine and horse serum albumin, also on mixtures of *l*-tyrosyl-*l*-tyrosine and 1,2-benzanthryl-10-carbamidoacetic acid.



IV

The absorption spectrum of *l*-tyrosine, the dipeptide, *l*-tyrosyl-*l*-tyrosine, and the tripeptide, *l*-tyrosyl-*l*-tyrosyl-*l*-tyrosine, have been measured recently[17] by one of the present authors. In a series of experiments, standard solutions of *l*-tyrosyl-*l*-tyrosine and horse serum albumin were prepared in a buffer solution at *p*H 8.0 and the observed curves compared with those calculated from the summation of the component curves for the two solutes. Three typical cases in which the concentration ratios of the *l*-tyrosyl-*l*-tyrosine to horse serum albumin were 1/2.3, 1/9.3, and 1/27.3 by weight are illustrated in Figs. 7–9. Over the whole concentration range a very satisfactory agreement between the experimental and the calculated curves is observed. In the neighborhood of the maximum at 2775A the agreement is excellent.

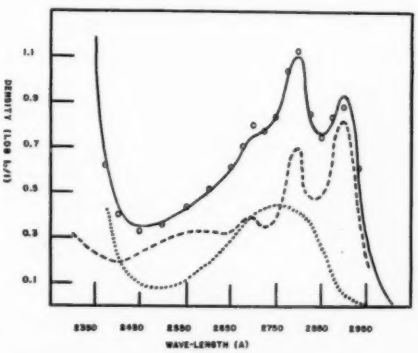


FIG. 10. Absorption spectrum of a mixture of *l*-tyrosyl-*l*-tyrosine and 1,2-benzanthryl-10-carbamidoacetic acid (concentrations of 57.7γ and 3.9γ per ml, respectively). (*A*) ——— Observed curve; (*B*) ····· Calculated curve for the *l*-tyrosyl-*l*-tyrosine component; (*C*) – – – – – Calculated curve for the 1,2-benzanthryl-10-carbamidoacetic acid component; ○ Points on the summation curve (*B*+*C*).

[16] Kindly supplied by Dr. W. F. Ross.

[17] To be published in a paper by W. F. Ross and A. E. Barkdoll.

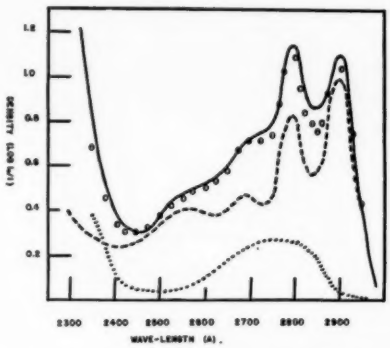


FIG. 11. Absorption spectrum of a mixture of *l*-tyrosyl-*l*-tyrosine and 1,2-benzanthryl-10-carbamidoacetic acid (concentrations of 34.6γ and 4.7γ per ml, respectively). Curves as in Fig. 10.

Similar experiments were carried out on solutions of *l*-tyrosyl-*l*-tyrosine and 1,2-benzanthryl-10-carbamidoacetic acid (Figs. 10 and 11) where, again, the calculated and experimentally observed absorption curves agreed satisfactorily. These results, insofar as they were applicable, substantiate the assumptions which Holiday has made, and suggest that the abnormal effects reported in the earlier sections of this paper are due to some mutual interaction of the chromophoric groups specific to the protein-carbamido hydrocarbon system under discussion.

CONCLUSIONS

It would appear from these observations that great care must be exercised in the application of ultraviolet spectrophotometry and colorimetry

to solutions containing proteins, as in certain cases serious errors may ensue. In the case discussed here, the method of analysis was developed as part of an investigation on the immunological protection against the action of carcinogenic substances. Provided the measurements of intensity are restricted to a certain wave-length range (3250–4000A), no serious errors are incurred; the discrepancies only become significant at shorter wave-lengths. The cause of the error has not been elucidated; it is possible that it only becomes significant at shorter wave-lengths because it is caused by some factor which is a function of the wave-length. On the other hand, the effect may be caused by some interaction between the chromophoric centers which is only significant when both chromophores are absorbing. If the latter should be the case, similar errors might be met with in the colorimetric analysis of substances in presence of pigmented proteins, such as the cytochromes, haemoglobins, and flavoproteins. These are conditions which may easily arise in clinical bio-chemistry.

ACKNOWLEDGMENT

The authors wish to express their appreciation of the advice and encouragement of Professor L. F. Fieser of Harvard University and to The International Cancer Research Foundation for financial support.

JOURNAL OF THE OPTICAL SOCIETY OF AMERICA VOLUME 33, NUMBER 4 APRIL, 1943

A New Spectroscopic Source Unit*

M. F. HASLER, *Applied Research Laboratories, Glendale, California*

AND

H. W. DIETERT, *Harry W. Dietert Company, Detroit, Michigan*

IN the ten summer conferences at Massachusetts Institute of Technology, two subjects have consumed a good portion of the time devoted to spectrochemical analysis: spectrographs with their attendant grating *vs.* prism arguments and spectral sources with their arc *vs.* spark arguments. In the case of the former, there is a difference of principle involved that allows no possible compromise, but in the case of the latter, the difference is largely of degree and hence should be reconcilable in the terms of a general best practice suitable for each analytical problem.

To date, however, this harmony has not been achieved, especially with respect to each expert's opinion of the best source for a particular job. This is largely due to the fact that a systematic study, starting with a highly damped spark of high voltage, which is known to be very spark-like in its character, and ending with a direct-current arc of high current, which is known to be very arc-like in its character, and including all possible cases in between, has never been made. To make such a study complete, all possible types of samples, ranging from metallic and non-metallic solids through liquids and gases, and all possible degrees of sample consumption, ranging from a few micrograms at a sample's surface to the whole sample should be included. This is a very ambitious research program, and one which is not even well begun at this time.

However, a method of attack that should yield answers to many questions of this nature quite readily has been developed. It is embodied in a new source unit that has many interesting features and possibilities. Before discussing this unit, it will be worth considering why it is so difficult, with conventional apparatus, to investigate the various discharge conditions that are intermediate between the arc and the spark.

Some definitions are necessary. A definition of an arc for spectrochemical analysis that may be

* Presented at the Tenth Summer Conference on Spectroscopy and its Applications held at the Massachusetts Institute of Technology, Cambridge, Massachusetts, July 20–22, 1942.

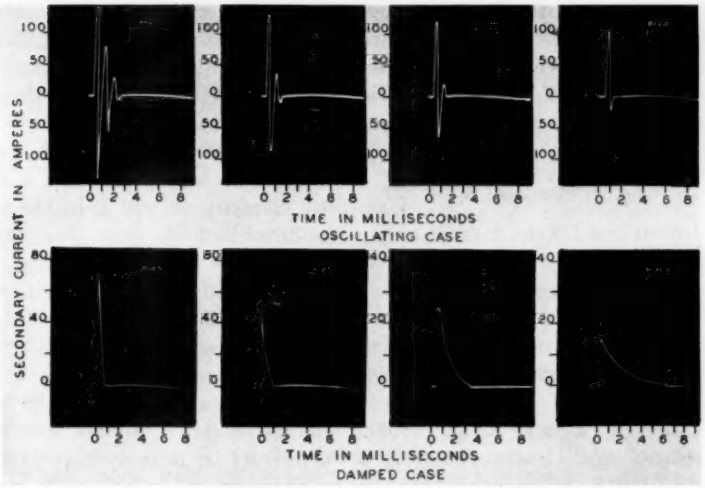


FIG. 1. Above—oscillograms of oscillatory discharges with increased damping as resistance is varied. Resistance of oscillating circuit 0, 0.53, 0.94, and 2.0 ohms, respectively. Below—oscillograms of damped discharges of increased duration as resistance is varied. Resistance of circuit 4.5, 9.5, 21.5, and 46.5 ohms, respectively.

suitable for the problem in hand is, that an arc is that part of a discharge which starts about one millisecond after an electrode gap has been broken down and continues for the duration of the discharge, providing the current is of the order of magnitude of amperes. The time, one millisecond, was chosen because it takes about this length of time for a discharge to achieve thermal equilibrium. Before that time the discharge is in a transition stage that starts with a spark and gradually converts to an arc. This is equally the case whether the discharge originates by applying a sparking potential between the electrodes, as in the spark, or by electrode contact as usually employed in the d.c. arc. The current of the order of magnitude of amperes insures that arcs suitable for spectrochemical analyses are being considered, arcs that allow the detection and measurement of elements at extremely small concentrations.

Definition of a spark is not an easy matter. In fact, it is such a controversial matter that no definition will be attempted at this time. However, everyone will agree that a discharge started between two separated electrodes, by the application of high voltage, is started by a spark. It is this phenomena that gives the name "spark source unit" to a well-known type of discharge used in spectrochemistry, despite the fact that the bulk of the discharge actually obtained and used, may be at low voltage.

The important point to be made here is not related to whether the discharge obtained from a conventional spark source unit is a true spark or not, but rather that the discharge obtained from such a unit is not, for practical analytical purposes, an arc and that a gap lies between the type of discharge obtained from so-called "spark" sources and those obtained from true arc sources.

To illustrate that gap, let us consider the high voltage alternating current spark unit in some detail. The spark unit, in its most common present form, consists of a high voltage transformer, providing from ten to forty kilovolts in the secondary, a condenser that is charged once every half-cycle by that voltage, and a discharge circuit connected across the condenser and consisting of inductance, resistance, and one or more spark gaps in series. Such a circuit is self-igniting in that the power stored in the condenser is at a sufficiently high voltage to break down the gap or gaps at a certain time in the charging cycle. Once the gap is broken down, the discharge proceeds independently of the charging circuit

and is dependent entirely on the values of C, L, and R, capacitance, inductance, and resistance, and upon the voltage E, to which the condenser was charged at the time of breakdown. The current passing through the gap is, neglecting gap resistance,

$$i = -(EC^{\frac{1}{2}}L^{-\frac{1}{2}})(e^{-Rt/2L})(\sin tL^{-\frac{1}{2}}C^{-\frac{1}{2}}),$$

where i is the current and t is the time after gap breakdown. The first term gives approximately the peak current for low damping; the second term, the damping, while the third term represents the oscillations. The upper left-hand oscillograph pattern of Fig. 1 illustrates this type of familiar relationship.

Starting with large E, C, and R; say 40,000 volts, 0.02 microfarad, and 15 ohms, small L, a few microhenries, and a synchronous gap in series with the analytical gap, a discharge will be obtained with a peak amperage of about 750 amperes, a duration of about 1.7 microseconds, giving three half-cycles of about 0.6 microsecond per half-cycle. Such a discharge we speak of as being very spark-like, irrespective of exact definition of the term used. The spectrum obtained shows a considerable enhancement of spark lines over arc lines for all elements detected as compared to that obtained from an arc for the same sample.

The spark characteristics of this discharge are due, first, to the high current densities available which allow multiple electron-atom collisions and thus excitation of atoms to very high energy states, and second, to the small concentration of electrode atoms of low excitation potential that prevail in the gap, because of the very short duration of the discharge. This small concentration of electrode atoms does not limit the electron velocities by inelastic collisions with these atoms to the extent that large concentrations would, and thus everything favors the production of very spark-like spectra.

If we consider this as one of the most spark-like cases obtainable with conventional apparatus, what modifications can be introduced to make the discharge more arc-like?

In the theory of oscillating circuits, the formula given holds only for $R^2/4L^2 < 1/LC$. If $R^2/4L^2 = 1/LC$ the circuit is critically damped and no oscillation occurs, while if $R^2/4L^2 > 1/LC$ the circuit is overdamped and just as in the critically damped case, only a single pulse of current results. Thus, two directions of change are possible in the apparatus discussed previously that will markedly change the current *vs.* time characteristics. The first is the usual one employed where $R/2L$ is made a great deal smaller by changing R and L in the circuit. R can be reduced to little more than the gap resistance, which is of the order of magnitude of an ohm, while L can be easily increased to 1000 microhenries. This changes the damping term enormously, thus lengthening the total time of discharge; likewise the maximum current—to 180 amperes, and the time per half-cycle—to 14 microseconds. If it were possible to charge the condenser to peak voltage and then let it discharge without interruption, a total time of discharge approaching a millisecond would be obtained for these circuit constants. Unfortunately the synchronous spark gap which must be used to allow the condensers to be charged to peak voltage, also limits the time of discharge due to its strong quenching action. Thus, though much more arc-like conditions can be obtained with a spark source unit under these conditions, than under those considered previously, arc conditions satisfying our definition are not obtained.

The other direction of change is to make $R^2/4L^2$ large compared to $1/LC$. Since we have considered about as small an L as possible in our first case, this can only be accomplished by increasing R. Increasing R to 20 ohms will provide the critically damped spark giving a trace similar to the lower left-hand oscillogram of Fig. 1. (The resistance and time shown on that trace do not apply to this case.) This discharge is unidirectional, at least for the duration of each spark. By increasing the resistance further, the maximum current would be dropped and the time of spark duration increased. The maximum time of discharge possible turns out to be about 100 microseconds, utilizing a resistance of ten thousand ohms. This gives a maximum current of a few amperes, which, over the short time available, provides only a small amount of luminous energy in the gap. This modification of the spark thus does not allow the production of true arc-like spectra, though it represents a trend in that direction.

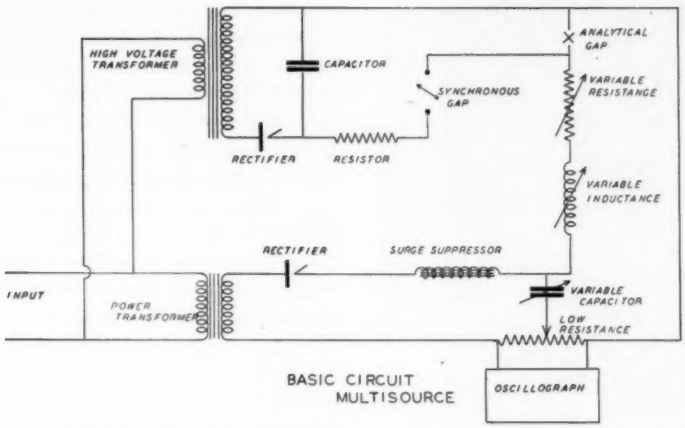


FIG. 2. Schematic wiring diagram of multi-source unit, showing the ignitor with synchronous gap above, and the power unit below with variable C, L, and R to the right, forming the discharge circuit.

Thus, one is forced to the conclusion that the conventional constants of the high voltage spark unit with synchronous gap are not such as to allow the production of true arc-like spectra. In fact, they are such that they do not allow much study of even the transitionary stages between spark breakdown of a gap and true arc conditions.

Before the discussion of sparks is concluded, one other development should be considered. This is the electronic spark generator of Malpica and Berry.[1] This unit was devised to control the spark in a manner different from the synchronous gap system. The term "control" is used to indicate that the condenser of the spark unit is charged to a very definite potential before the discharge is initiated. In the usual spark system, the charging is terminated by initiating the discharge at a very definite point on the voltage cycle by means of the synchronous spark gap. Besides initiating the discharge, however, the synchronous gap also terminates the discharge, due to its strong quenching action. In the electronic spark generator, on the other hand, a definite charge is stored in a large condenser in the primary circuit and triggered through the primary of the high voltage transformer with an ignitron. This "measured" pulse is used to charge the usual high voltage condenser in the secondary circuit to a sufficiently high voltage so that the gap breaks down. The spark produced then terminates with the discharge of the condenser. The high reproducibility obtained, which appears on a par with the best conventional spark unit work, proves that, at least for certain values of L, C, and R, termination of the discharge by a synchronous gap is of no significance. If this proves to be true in general, and our tests indicate that it may be, then uniform discharges of appreciably longer duration can be achieved for a given L, C, and R if only "controlled" charging is employed and the discharge is allowed to proceed to its natural termination.

To round out the preliminary discussion, what of arcs? Can their characteristics be extended to take in more spark-like conditions of discharge? The most promising approach to this side of the problem is study of interrupted arcs of short duration—the time "on" being adjustable from the continuous arc state through durations of milliseconds and finally to hundreds and tens of microseconds.

The usual a.c. arc, developed by Duffendack,[2] having a duration of from four to six milliseconds and an average current of from one to ten amperes, comes under the category of an arc by our definition. It may be termed a "spark-ignited" arc.

[1] J. T. M. Malpica and T. M. Berry, Gen. Elec. Rev. 563–65 (Oct. 1941).

[2] O. S. Duffendack and R. A. Wolfe, *Proceedings of the Fifth Summer Conference on Spectroscopy and Its Applications* (John Wiley and Son, New York, 1938), pp. 24–27.

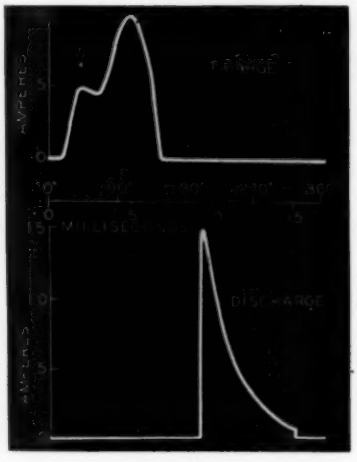


FIG. 3. Oscillograms of charge and discharge current, showing the complete independence of each when the discharge is initiated during the alternate half-cycle from the charge.

The questions that this discussion should raise are as follows: First, can a circuit be developed that charges a condenser to a definite voltage before each gap breakdown, thus insuring reproducibility of the quantity of electricity available for each discharge? Second, can one be developed that has only the analytical gap in the discharge circuit, thus allowing the termination of the discharge to be dependent only on the circuit and gap constants? Third, can one be developed that has suitable values of inductance, capacitance, and resistance so that discharges both oscillatory and undirectional can be varied from time durations similar to those obtained with the ordinary spark unit to durations of milliseconds, to give a wide variety of excitation conditions ranging from spark to arc?

We believe that such a circuit has been developed and that the controlled multi-source unit built around it should allow improvements of many spectrochemical procedures besides allowing a great advance in our knowledge of discharges.

The basic circuit diagram of the unit is shown in Fig. 2. In the upper portion of the diagram is the high voltage ignitor, while the lower portion depicts the high powered, low voltage rectifier used to charge the condenser bank. The ignitor discharges across the analytical gap through a synchronous gap and a resistor, while the large condenser bank discharges through the analytical gap, once it has broken down, through a power resistor and an inductance.

This general circuit charges the power condenser—also the ignitor condenser—to a very definite peak voltage on one-half of the cycle and then allows the condenser to stay charged until needed for the discharge period, during the next half cycle. This complete separation of charge and discharge period makes each independently controllable. Figure 3 shows an oscillogram of the charging current above and an overdamped discharge below. The fact that the current drops to zero between the conclusion of the charge and the start of the discharge, indicates clearly their complete independence. The point of initiation, during the cycle of the discharge, is adjustable with the synchronous gap in the ignitor circuit. Though this point can be adjusted with great precision, it is of small significance as long as the discharge starts after the charging has ceased and ends before the next charging begins. This is in contradistinction to the usual synchronous gap adjustment where it determines the exact voltage to which the condensers are charged.

By using an ignitor in parallel with the main power unit across the analytical gap, breakdown of the gap can be performed with a low powered ignitor circuit, the constants of which in no way effect the main discharge. This provides the

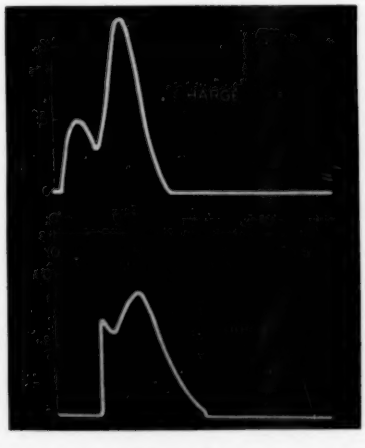


FIG. 4. Oscillograms of charge and discharge when the discharge is initiated during the charging period.

great advantage mentioned previously of allowing relatively long discharges the duration of which depend only upon the power circuit and gap constants. A practical advantage of this arrangement is that the synchronous gap only carries the low power of the ignitor circuit and hence its sparking electrodes should have a very long life.

By utilizing relatively low voltages in the power circuit, it is feasible to employ very high values of capacitance. This allows overdamped discharges to be employed which possess long time constants and which pass large amounts of energy through the analytical gap. Thus, this type of discharge, which was impractical in the case of the standard spark unit, due to the capacitance available, now becomes a practical mode of operation.

Thus, such a circuit fulfills very well all of the requirements previously discussed. The usual limitation in time constants associated with the conventional spark source is entirely eliminated. Figure 1 shows oscillatory discharges of several milliseconds duration, followed by a critically damped discharge and several overdamped discharges as the series resistance of the circuit is increased. Figure 4 shows what happens when the phase of the initiator is changed 180° so that it causes a discharge to be initiated during the charging cycle of the power circuit. This produces a discharge, the duration of which may be controlled by the time of initiation. An interesting combination of the over-damped discharge and this last discharge is shown in Fig. 5. This gives a thirty-cycle discharge of very long duration—up to sixteen milliseconds.

With such a source available, the first question is, what is the appearance of the spectra of discharges that are intermediate between the arc and the spark? Some of the more obvious points may be brought out by inspection of Fig. 6. To be consistent with the rest of our exposition, we should have started out with a highly damped spark of very short duration and by increasing the inductance and decreasing the resistance, show how longer and longer oscillating discharge periods are obtained, and how the spectra become more and more arc-like. Another series of results should start out with the critically damped case and by increasing the resistance show how longer and longer unidirectional-discharge periods are obtained. It happens to be very convenient to telescope both of these studies into a single series by varying only one parameter, resistance R. If we start with low resistance and gradually change to high resistance, we start out with the arc-like oscillating case, progress backward to the critically damped spark-like case, and then again pass through more and more unidirectional arc-like cases. Figure 1 shows a typical series of this type where the series resistance has been changed systematically to give the discharge shown by the oscillograms. Figure 6 shows the series of spectra obtained under those conditions. The exposures have been adjusted so that an arc line of about seven electron volts excitation energy has about the same degree of blackening all through the various spectrograms.

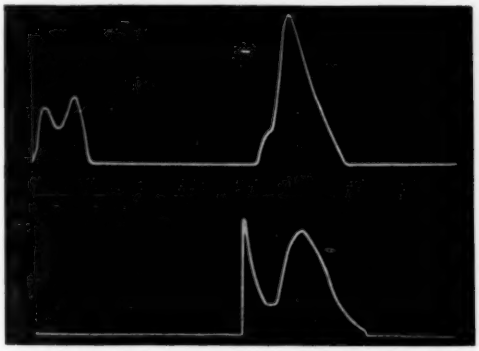


FIG. 5. Oscillograms of charge and discharge when the discharge is initiated after the condensers are charged, but immediately before the next charging cycle, so that the charging power contributes to the later portions of the discharge. This produces a thirty-cycle discharge of very long duration.

The first four spectra indicate how an oscillating discharge is made more spark-like by increasing the resistance; the fifth represents the critically damped case, while the last three represent unidirectional discharges of longer and longer duration, producing more and more arc-like spectra as the resistance is further increased. The very wide variation of discharge conditions possible is particularly noticeable in the last four spectra.

The intensity ratios of certain lines have been measured in order to illustrate clearly how the line intensities of singly and doubly ionized

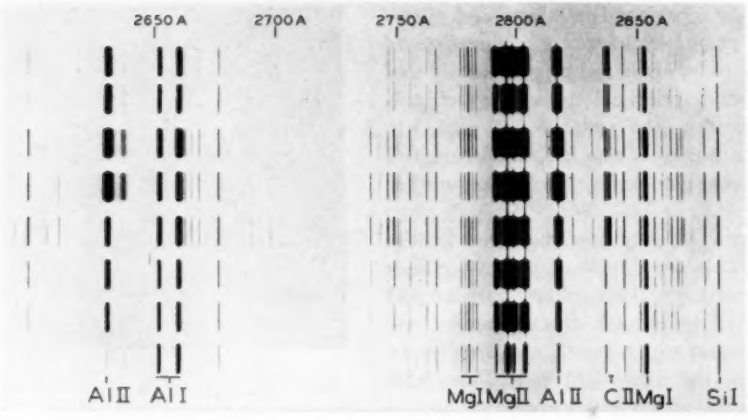


FIG. 6. Spectrograms of aluminum taken under a variety of discharge conditions, following from top to bottom, the sequence depicted in Fig. 1. Top electrode aluminum, bottom wedge-shaped carbon, capicitance 40μf, inductance 362μh.

Spectrogram	Type	Resistance (with gap)	Duration
1	Oscillating	0.5	2.25 milliseconds
2	Oscillating	1.0	1.5 milliseconds
3	Oscillating	1.5	1.0 millisecond
4	Oscillating	2.5	.7 millisecond
5	Unidirectional	5.5	.5 millisecond
6	Unidirectional	10.5	1.0 millisecond
7	Unidirectional	20.5	3.0 milliseconds
8	Unidirectional	40.5	6.0 milliseconds

aluminum atoms vary with respect to neutral atom lines as discharge conditions are changed. These are shown in Fig. 7 in the form of curves relating intensity ratio to resistance in the oscillating circuit. The maxima of these curves indicate the most spark-like conditions of discharge. It was rather surprising to find these maxima on each side of the critical damping resistance of about 5 ohms, as the high currents and short duration of the discharge of this resistance would lead one to expect it to be the most spark-like of all. This anomaly appears to be linked to the other electrode, a carbon rod in this case, held below the aluminum disk, and made the cathode in the unidirectional cases. Carbon lines and bands were greatly enhanced in this spectrum as compared to aluminum lines.

Other points of interest are the fact that lines originating in such high energy levels can be excited by less than a thousand volts across the analytical gap, and the finding that oscillating discharges of the same total duration are considerably more spark-like than unidirectional discharges. This last appears to be related to the higher amperage utilized and the oscillating character of the current. These findings indicate that our simple definition of an arc, though it sufficed for orientation purposes, must be modified and amplified to meet the more complicated facts of experiment. Experiments are being continued along the above lines which should throw much light on discharge mechanisms in general.

Figure 8 shows the pattern left by the discharge on an aluminum standard disk. This disk was the upper electrode of the discharge and was positive in the unidirectional cases. The lower electrode was a wedge-shaped carbon one, separated from the upper by a three-millimeter gap. It is apparent that the oscillating discharges obtained with low resistance in the circuit—the value of which is indicated by the numerals of the figure—are large and powerful, blowing electrode material about to a considerable extent. The overdamped discharges, on the other hand, being unidirectional and quite sustained, make orderly patterns that reflect the shape of the lower wedge electrode.

What are the facts with respect to the sensitivity of this source for the detection and measurement of minute concentrations of ele-

ments in various matrices? This subject has barely been touched but the examples investigated have been very encouraging. The results for aluminum are shown in Table I. Here the most sensitive cases of discharge of all the possible types are compared. The first column shows the overdamped case, the second the oscillating case of long duration, the third the 60-cycle pulsating discharge, and the fourth, the 30-cycle combined discharge. The oscillograms of these cases were shown in Figs. 3, 1, 4, and 5, respectively. The high sensitivities obtained indicate the true arc-like character of all four of these discharges.

In analytical work the emphasis is often not on sensitivity, but on accuracy. Of all the discharges discussed, the overdamped discharge should be the most reproducible. Looking at Fig. 3 again, it is apparent that if we have a

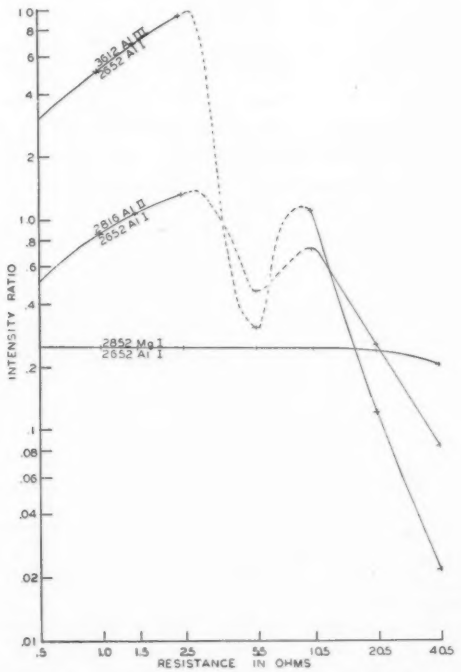


FIG. 7. Intensity ratios of various spectrum lines showing the wide variety of discharge conditions obtainable with the multi-source unit.

Spectrum lines	Excitation potential in electron volts
3612 Al III	42.4
2816 Al II	17.7
2652 Al I	4.7
2852 Mg I	4.3

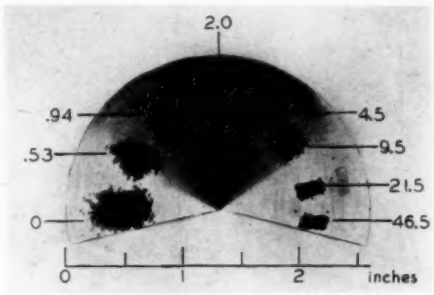


FIG. 8. Photograph of the discharge patterns obtained on aluminum disk when used as the upper electrode opposite a wedge-shaped lower electrode of carbon. Numbers indicate resistance in oscillating circuit and correspond to sequence of Figs. 1 and 6.

means for measuring and controlling the peak voltage to which the condenser is charged, exact equality of discharges should result even if ignition should occur at slightly different points in the cycle. Also referring to this discharge's electrode pattern, it appears as a good reflection of the lower electrode shape, showing that no excess wandering of the discharge about the specimen surface occurs. These facts, coupled with the continuous flow of analytical vapor away from the sample during each discharge, seem all to point toward a perfect set-up for high reproducibility. If such be the case, then high sensitivity certainly cannot be held against it, particularly when that sensitivity is controllable to a great extent.

Table II shows the degree of reproducibility obtained in the intensity ratios of lines of various elements to one of aluminum on eight repeat runs. Each spectrogram was produced by repeating a five-second predischarge and a ten-second exposed discharge twice. This was done to minimize sampling errors, with the hope that only source and photographic errors remain. The reproducibility obtained appears very acceptable, particularly in view of the extreme percentages involved, and compares favorably with conventional spark sources, *despite the fact that the discharge is much more arc-like in character than can be obtained from the above-mentioned sources.*

Besides high sensitivity in the detection and measurement of trace elements and high reproducibility, there is another quality that a discharge must possess in order to be useful in the

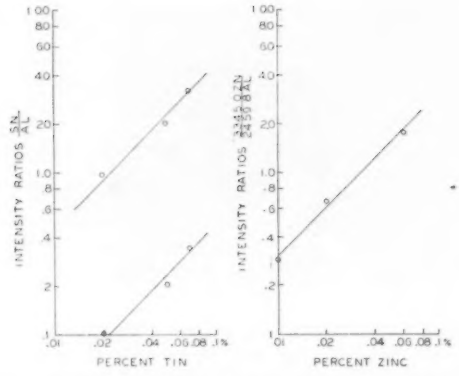


FIG. 9. Working curves for tin and zinc at low percentages showing how the points fall on a 45° line which indicates a linear relationship between intensity and concentration.

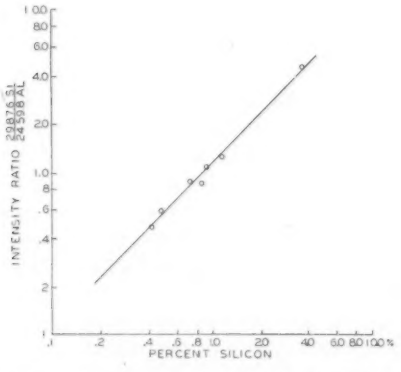


FIG. 10. Working curve for silicon showing a linear relationship between intensity and concentration over a tenfold range of values.

solution of a wide variety of analytical problems. That property is a large change of line intensity with change of element concentration. Theoretically, the perfect discharge, in this respect, is one that shows no self-absorption and therefore a linear change of line intensity with concentration. Such a relationship appears as a straight line at 45° when log [I (element to be measured)/I (standard element)] is plotted as ordinate against log concentration as abscissa. Figure 9 shows this in the low percentage region 0.01–0.1 percent, where such relationships usually are obtained. Figures 10 and 11, on the other hand, refer to amounts up to four percent. Off hand, this may not appear very significant, for when weak lines that start and end in high enough energy states are used, little self-absorption is to be expected in any kind of a discharge. However, the great length of the linear portion of the line in the copper case, almost a hundred-fold in intensity and concentration, attests to the true smallness of self-absorption in this type of discharge.

So far, the discussion has centered about aluminum and its analysis. Can a single source take the place of the high voltage spark and the a.c. arc in the case of other metals and nonmetallics, and at the same time simplify the spectrum and extend the usefulness of new lines to such an extent that spectrographs of medium dispersion will suffice for even stainless steel analysis? The answer, we believe, is yes. Figure 12 shows a series of spectrograms from discharges on a steel sample obtained by increasing resistance in the circuit. The trend to a clean-cut simple arc spectrum at the bottom of the figure is very marked, while the high sensitivity is indicated by the chromium line at 4254.3A, which is much too dense for measuring purposes for the 0.02 percent chromium in the sample. This line can be used to detect and measure chromium at 0.001 percent in the most favorable discharge. Many other arc lines exist which can be used to measure very low percentages of most alloying constituents in steels. These lines, together with others suitable for higher percentage analysis, are shown in Table III. The

TABLE I. Sensitivity of various sources for aluminum analysis. Sensitivity given is in percent composition for line intensity equal to three-tenths background intensity.

	Description of discharge	Type	Frequency
S_1	Separate charge; overdamped discharge	Fig. 3	60 cycle
S_2	Separate charge; oscillating discharge	Fig. 1–1	60 cycle
S_3	Overlapping charge—discharge	Fig. 4	60 cycle
S_4	Overlapping charge—discharge	Fig. 5	30 cycle

	Circuit constants				
	C	L	R	Peak current	Duration
S_1	40 μf	362 μh	46.5 ohms	15.4 amp.	5,500 μsec.
S_2	5 μf	362 μh	0.5 ohms	71.0 amp.	630 μsec.
S_3	20 μf	362 μh	75.0 ohms	9.5 amp.	6,500 μsec.
S_4	20 μf	362 μh	75.0 ohms	10–9 amp.	16,000 μsec.

Element	Line	S_1	S_2	S_3	S_4
Chromium	4254.3	0.0005	0.007	0.002	0.002
Copper	3247.5	.0003	.0002	.0001	.0001
Iron	3020.6	.002	.006	.002	.002
	2382.0	.01	.004	.01	.01
Magnesium	2852.1		very sensitive		
	2783.0	.005	.05	.007	.01
Manganese	4030.8	.0008	—	.0006	.0007
Molybdenum	3170.3	.003	.01	.001	.002
Nickel	3414.8	.0005	.001	.0003	.0003
Lead	2833.1	.002	—	—	—
Silicon	2881.1	.002	.008	.003	.003
Tin	3175.0	.002	—	—	—
Titanium	3372.8	.001	.001	.0006	.001
Zinc	3345.0	.002	.005	.002	.002

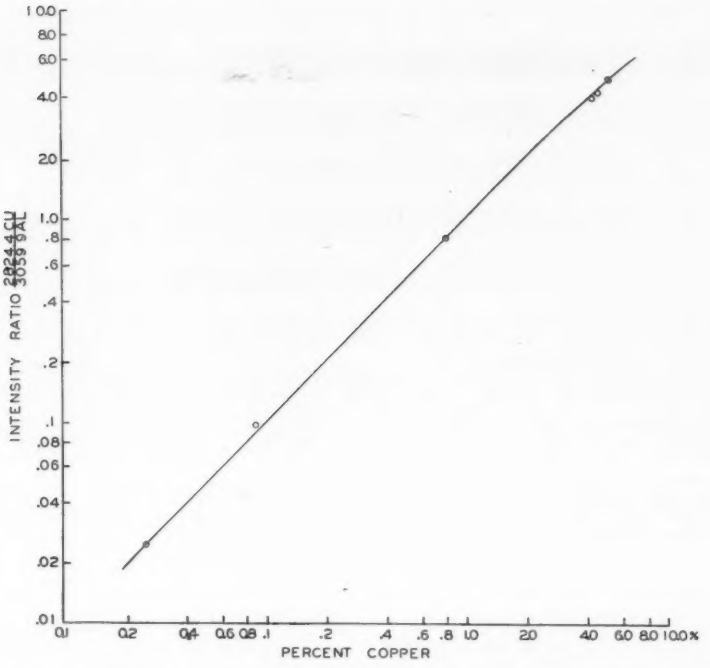


FIG. 11. Working curve for copper, showing almost a linear relationship between intensity and concentration over a two-hundred-fold variation of values.

important point to be made here is that steel and iron products can be analyzed with high precision with a very arc-like source which produces a spectrum that is simpler and more sensitive than the spark spectrum usually employed. A large number of lines are free from any possible interference when a grating spectrograph of only medium dispersion is used in conjunction with such a source. Even in the case of the 2881.6A silicon line, which has a weak spark chromium line next to it at 2881.9A; this line is usable without any correction up to chromium percentages of 20 percent, thanks to the arc-like

TABLE II. Reproducibility of intensity ratios —aluminum alloy.

CIRCUIT CONDITIONS

Capacitance	40 microfarads
Inductance	362 microhenries
Resistance	46.5 ohms

Eight repeat analyses with aluminum disk above, wedge-shaped carbon electrode below.

Element	Line ratio	Composition—Percentage present	Intensity ratio Percentage deviation from mean
Chromium	4254.3/3059.9	0.01	1.9
Copper	2961.2/3059.9	.79	1.2
Gallium	2943.6/3059.9	—	1.6
Iron	2382.0/2459.8	.15	1.9
Magnesium	2783.0/2459.8	.25	1.5
Manganese	4030.8/2459.8	.02	2.4
Nickel	3414.8/2459.8	.01	2.3
Silicon	2987.6/2459.8	3.70	1.4
Titanium	3372.8/3059.9	.01	4.1
Zinc	3345.0/2459.8	.01	1.6

TABLE III. Lines suitable for low or high alloy iron and steel analysis when very arc-like discharge conditions are employed.

Element	Very low percentage analysis	High percentage analysis
Chromium	4254.3A	4511.9A
Manganese	4030.8A	4451.6A 4453.0A
Nickel	3414.8A	4331.6A
Silicon	2881.6A 2516.1A	3905.5A
Molybdenum	3864.1A	2816.2A
Vanadium	4379.2A	

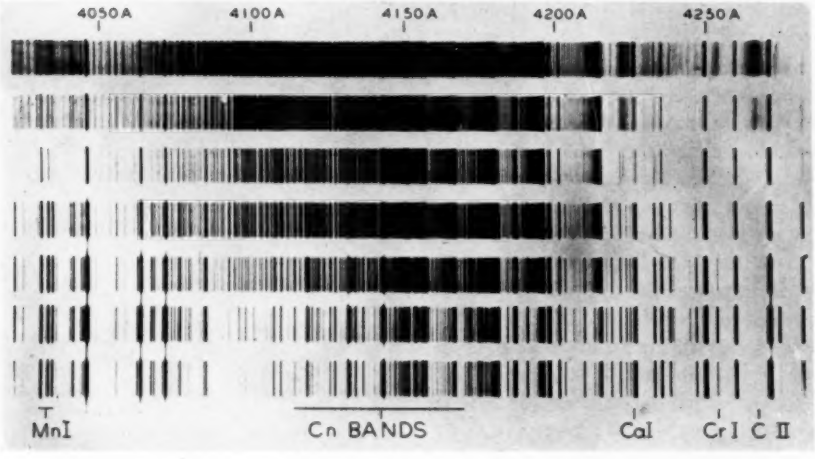


FIG. 12. Spectrograms of steel taken under a variety of discharge conditions. Resistance increasing from top to bottom producing more and more arc-like spectra. Steel, lower electrode; carbon, upper electrode.

character of the discharge, which suppresses this spark chromium line to a large extent.

No report, even a preliminary one, of a source of wide applicability is complete without discussing the analysis of non-metallic samples. During the last few years our laboratories have done a great deal of work on the analysis of non-metallics[3] for both major and minor constituents by means of the spectrograph. In all this work, an ordinary d.c. arc unit was employed as the source, the innovation being to use specially shaped electrodes and an alkali carbonate flux to insure melting and decomposition of the sample before it entered the discharge. Another feature of the method is completely to consume the sample and that portion of the electrode with which the sample has come in contact. Because of our previous successes we tried to use this technique "as is," with the new source. The results obtained to date, though meager, have been very gratifying. The time to consume the sample, plus electrode, with the ordinary d.c. arc adjusted to 7½ amperes is 80 seconds. It was thought that due to the intermittency of the new source, considerably longer times would be necessary for the available power. However, the time of consumption turned out to be identical when a peak current of ten amperes was obtained in the overdamped discharge. Thus, the conclusion appears justified that this unit can replace the d.c. arc in non-metallic analysis, bringing to that work the advantages of sixty-cycle ignition and control.

The authors wish to acknowledge their indebtedness to J. W. Kemp, of the development staff of Applied Research Laboratories, for carrying through a large portion of the practical testing and designing of this unit.

[3] Lecture presented at the 1941 meeting of American Association for the Advancement of Science, Dallas, Texas, entitled "Quantitative Spectrochemical Method for Non-metallic Sample Analysis" by M. F. Hasler.

JOURNAL OF THE OPTICAL SOCIETY OF AMERICA VOLUME 33, NUMBER 4 APRIL, 1943

The Measurement of Transmission and Contrast in Optical Instruments*

D. B. McRae
Eastman Kodak Company, Rochester, New York

OPTICAL instruments of many kinds are today being produced in greater quantities than ever before, and tests for the quality of their performance are naturally of the greatest interest to both the manufacturer and to the user, the latter being, in most cases today, one of the country's armed services.

Testing methods for aberrations of lenses, correctness of prism angles, accuracy of optical surfaces and proper adjustment of instruments are fairly well known and their application is quite extensive, and much of the literature on these subjects has found its way into textbooks. Besides these questions, however, the optical designer is much interested in the question of getting the maximum possible light flux through the instrument.

War seems to be quite effective in stirring up interest in the transmission of complicated optical instruments. This is quite understandable because in peace time we are apt to content ourselves with relatively simple optical systems in which the transmission has reasonably high values and the question of possible improvement is not too serious. War brings with it the need for very complex sighting instruments containing astonishingly large numbers of glass-air surfaces, and having very large light losses. There promptly arises a need of methods of accurately measuring the light actually transmitted by various instruments.

World War I was responsible for a series of papers dealing with transmission measurements, and the interest has continued to some extent down to the present time of World War II, which has sent many of us scurrying to the literature to refresh our minds on the subject. It is the purpose of this paper to collect and review the more important papers dealing with the subject of transmission measurements, which have appeared in the literature, bearing in mind that it will only be possible to discuss some of the most outstanding material without exceeding the bounds of reasonable space. For the benefit of those who are interested in further details, a more complete bibliography will be found at the end of the paper.

The basic physical relations which determine the maximum possible light flux which can pass through an instrument, and the brightness of the image formed by such a system have been ably discussed by various writers and an excellent textbook treatment has been given by Hardy and Perrin.[55] The results, however, are the maximum possible results which could be expected from a perfect optical system, i.e., one in which lenses are considered to refract rays of light without any losses. Unfortunately, real lenses not only perform their appointed duties as refractors of light but they also reflect, absorb, and scatter, with the result that in some complex optical systems, the emergent light may be only 20 percent of that predicted by the theory of flux distribution. Martin[56] has also discussed the problem, introducing a constant to take account of such losses.

In some of the simplest cases it is possible to make approximate calculations of losses by reflection and absorption, but for more complex instruments, a transmission factor, which may be defined as

$$K=\frac{I-(L_A+L_R+L_S)}{I} \qquad (1)$$

must be determined experimentally. In the above formula:

L_A = loss by absorption,
L_R = loss by reflection,
L_S = loss by scattering,
I = incident light.

Occasionally, it may be possible to distinguish between the various losses, but usually it is possible to determine only their sum.

The measurement of the transmission factor of instruments does not appear to be as well known

* Paper presented by invitation at the Symposium on Optical Instruments at the Twenty-Seventh Annual Meeting of the Optical Society of America, New York, New York, October 30–31, 1942.

as the tests for image perfection and the tests for proper surface geometry. This may perhaps be ascribed to a comparative lack of interest along these lines. Articles dealing with this subject have appeared from time to time in the literature, but general interest was perhaps not aroused because there seemed to be very little that one could do to improve the transmission factor. In most cases the design of the instrument was pretty well determined by other considerations, and it was necessary to accept the transmission at whatever value it turned out to be.

It was known that it was possible to decrease reflection by treating glass surfaces with various chemicals, and Kollmorgen[6] had reported success in thus treating the surfaces of all kinds of optical glass, and had further pointed out the greatly increased transmission resulting from the use of such treated glass in periscopes. His methods were not published, however, and others were unsuccessful in attempting to attain his results.

During the last few years a number of methods of producing low reflectance surfaces on glass have been discovered, and this has undoubtedly been responsible for a revival of interest in the transmission factor of optical instruments, inasmuch as it is now possible to exercise considerable control over this factor.

HISTORICAL

There is evidence that something was known regarding the measurement of the transmission of lenses prior to 1900, although it has proved a bit difficult to locate actual descriptions of methods used. Some of the fundamental principles were described by Bouguer,[62] and Lambert,[63] in 1760. Bouasse[57] describes an arrangement used by Lambert.

In 1902, H. Kruss[1] published a paper in which he discussed the brightness of telescope images. He pointed out the fact that the image seen through a telescope has the same brightness as would be seen by the eye viewing the object directly, were it not that some light is lost by reflection and absorption. In the following year, the same author published another paper[2] in which he dealt with the subject of light losses and their dependence on the construction of the instrument, and kinds of glass used. He described an arrangement for measuring the loss of light in binoculars by separating them into two parts and placing the parts end to end with the eyepieces together.

Little further interest appears to have been taken in the subject until some ten years later when R. W. Cheshire[3] described in some detail a photometer arrangement devised by him for measuring the transmission of photographic lenses. He calculated the reflected-light loss of several lenses by means of the Fresnel equations, and then finding that the measured losses were somewhat in excess of this amount, he attributed the discrepancy to absorption. By working with a number of lenses having different total glass thicknesses, he came to the conclusion that absorption amounted to about 2.4 percent for each centimeter of axial thickness of glass in the lens.

In 1919 a paper was published by F. E. Wright[10] concerning methods he had used during the war period for the measurement of transmission of optical glasses and optical instruments. This paper is chiefly valuable for a discussion of various ways of using polarization photometers for the measurement of transmission and absorption* of optical glass in the form of flat plates. This problem is treated in considerable detail. Other applications of the instrument to the measurement of reflectivity, transmission of optical instruments, and the measurement of sky polarization are mentioned quite briefly, with rather inadequate illustrations. A following paper[11] discussed the design of polarization photometer prisms, and suggested a method of using a calcite cleavage rhomb in place of the Wollaston prism, when the latter proved difficult to obtain.

During the following years quite a number of papers dealing with the photometry of optical systems have appeared. Two of the most important are those by Guild,[13] and by Moffitt and Taylor.[17] Many of the later papers have dealt to some extent with the subject of errors in transmission measurements. Others have discussed the use of other types of photometers. Quite a number of the papers are in French and Italian journals.

---

* A rather comprehensive study of the absorption of various optical glasses has been given by Haigh, reference 39.

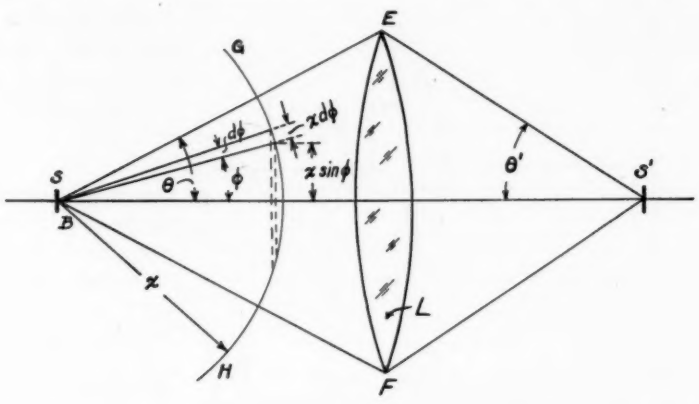


FIG. 1.

THEORY AND METHODS OF MEASURING TRANSMISSION

All measurement of the light transmitted by optical instruments is based upon one fundamental equation for image brightness. If a plane light source is imaged onto an image plane by a lens, or system of lenses, the illumination at the center of the image is given by:

$$E' = \pi B (N'/N)^2 \sin^2 \theta' \tag{2}$$

in which we have

B = brightness of object plane,
N' = refractive index of final image space,
N = refractive index of object space,
θ' = slope angle of the most oblique ray which passes from the extreme edge of the lens to the axial image point.

The derivation of the equation is not difficult. In Fig. 1, S is a small plane surface of brightness B. Light radiated from S in a cone of half-angle θ just fills lens L and is refracted to form the image S'. To find the total flux in the cone SEF, describe an imaginary spherical surface GH, with center at S, and of radius x. Then consider the element of flux contained in the thin conical shell with inner angle ϕ and outer angle $\phi + d\phi$. This shell cuts GH in an annular ring of width, $x d\phi$ and radius $x \sin \phi$. The area of the ring is $(x d\phi)(2\pi x \sin \phi)$ or $2\pi x^2 \sin \phi d\phi$. The illumination on this area is $AB \cos \phi / x^2$, where A is the area of the source S. The elementary flux passing through the area is, then:

$$\begin{aligned} dF &= (AB \cos \phi / x^2) 2\pi x^2 \sin \phi d\phi \\ &= (\pi AB)(2 \cos \phi \sin \phi d\phi) \end{aligned} \tag{3}$$

and the total flux in the cone of the half-angle θ, is:

$$\begin{aligned} F &= \int_{\phi=0}^{\phi=\theta} dF \\ &= \pi AB \sin^2 \theta. \end{aligned} \tag{4}$$

Denoting the area of the image S' by A' we find the illumination on S' is:

$$E' = \pi (A/A') B \sin^2 \theta. \tag{5}$$

According to the sine condition, which is fulfilled by most lenses, the ratio of the areas can be expressed as

$$\frac{A}{A'} = \frac{N'^2 \sin^2 \theta'}{N^2 \sin^2 \theta}. \tag{6}$$

This, when substituted into the previous equation, gives Eq. (2).

This is essentially the treatment given by Martin. Hardy and Perrin have given a more extended discussion in which they have shown that this equation is true not only at the focused image but at all points along the axis of the lens, or instrument. One must be careful in this case to be certain that he is using the correct value of θ' for the point in question, as in some cases this is limited by the size of the image S' rather than by an aperture stop.

Almost all instruments with which we have occasion to deal have both object and final image in air. The ratio N'^2/N^2 is, in this most usual case, unity, and Eq. (2) simplifies to the form:

$$E' = \pi B \sin^2 \theta'. \tag{7}$$

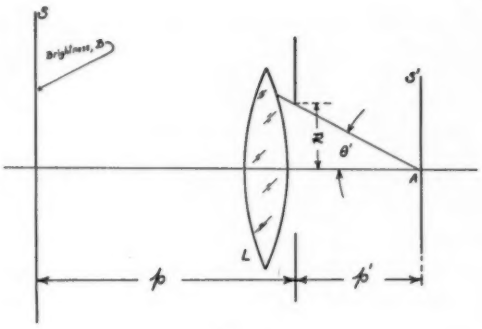


FIG. 2.

We learn then that the image illumination is dependent on only two variables, first, the brightness of the source, and second, the slope angle of the most oblique ray reaching the axial image point. In particular, we note that nothing is said regarding the distance of the object or the magnification of the system. Three assumptions have been made, however, in deriving the equation. They are:

1. The source (object) emits light according to Lambert's law.
2. The lens system fulfills the sine condition.
3. The lens is perfectly transparent, so that no light is lost by absorption or reflection.

In most cases we may safely assume that no extensive departures from Lambert's law exist within the angles of interest, and long hours of labor on the part of the lens designer assure us of freedom from coma, so that the second assumption may be regarded as correct.*

Assumption number three, however, is never valid as actual lenses do cause considerable loss. It is necessary, therefore, to modify our fundamental equation to take this into account. If we denote the ratio of the light flux emerging from a lens (or optical system) to that incident upon it by the symbol, k, we have as our basic equation:

$$E' = k\pi B \sin^2 \theta'. \tag{8}$$

One might say that this equation contains all of photometry. Certainly, it is the most important equation in that subject.

Optical instruments whose transmission we are apt to want to measure may be divided into three broad catagories:

1. *Systems which have a finite focal length* and are capable of forming on a screen a real image of a more or less distant object. This class includes camera lenses of all descriptions and such things as telescope objectives considered as individual items apart from their assembly in an instrument.

2. *Systems which are "afocal."* Telescopes of many varieties come under this classification, e.g., gunsighting telescopes, rangefinders, binoculars. This class is distinguished by the fact that sensibly parallel light arriving at one end of the device passes through and emerges from the other end still parallel. The apparent angular subtense of two separated points of the object may or may not be altered, depending on the magnifying power of the telescope.

3. *Dispersing Systems*—monochromators, etc.

SYSTEMS OF FINITE FOCAL LENGTH

We may take first an elementary case of type I, which is a simple positive lens. In what way can our fundamental equation enable us to measure its transmission factor? Let us consider the arrangement of Fig. 2. If we have a large plane source of light S of brightness B, and form its

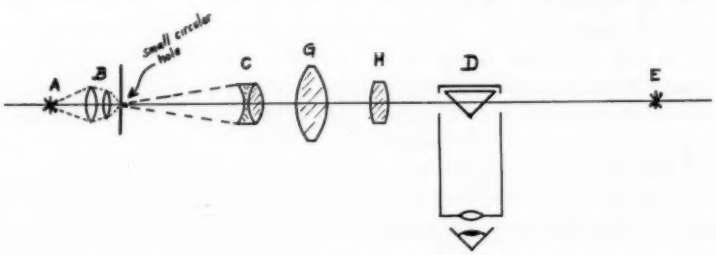


FIG. 3.

* It is of interest to note, that Slussareff, reference 51, in a detailed study of the distribution of light in the image plane, has shown that the presence of coma markedly alters the usual distribution, and that by a suitable use of coma, distortion and field curvature, it is possible to overcome the normal falling off of illumination from center to edge of field.

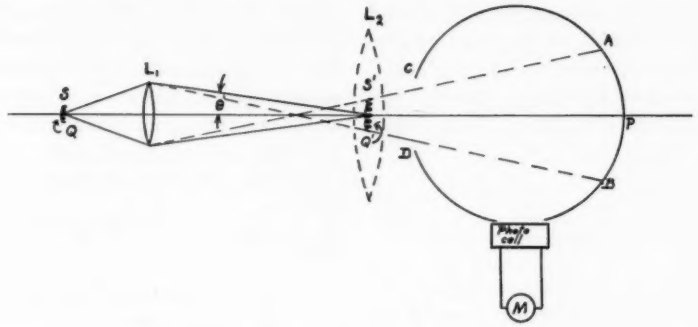


FIG. 4.

image S' on a screen by means of lens L, which has behind it a diaphragm of radius R, we find the illumination at A is:

$$E_1' = k\pi B \sin^2 \theta'. \tag{9}$$

The lens is now removed, leaving the diaphragm unchanged. The slope angle of the extreme ray to A is still θ' and so the illumination at A is:

$$E_2' = \pi B \sin^2 \theta' \tag{10}$$

provided that the source S is large enough so that the most oblique ray reaching A, with lens removed, is determined by the edge of the diaphragm, and not by the edge of S.

Divide Eq. (9) by Eq. (10) and we get

$$\frac{k\pi B \sin^2 \theta'}{\pi B \sin^2 \theta'} = \frac{E_1'}{E_2'} = k. \tag{11}$$

We thus have a simple way of measuring the transmission factor of a lens, which, it is interesting to note, has been attributed to Lambert.

The details of the arrangement could be worked out in many ways. Instead of measuring the ratio of the illuminations with and without the lens, one could use a diaphragm whose radius can be changed. After making an illumination measurement with the lens in place it could be removed and the diaphragm closed down until the illumination on A attained its previous value. The transmission of the lens would then be given by the ratio

$$k = \sin^2 \theta_2' / \sin^2 \theta_1', \tag{12}$$

where θ_2' is the value of the angle without the lens, and θ_1' is the value of the angle with the lens in place. For small values of θ', this ratio would be substantially equal to the ratio R_2^2/R_1^2, which would be easier to measure than the sines. It would also be possible to have two similar diaphragms and screens, to be illuminated by a common source S. The lens could then be placed in position over one of the diaphragms, and the respective illuminations measured, or brought to equality by varying one of the diaphragms. This would have the advantage of eliminating the effect of variation of the brightness of the source with time.

The illumination at point A could be measured by one of the various types of visual illuminometers, or a small hole of fixed size might be made at A to admit light into an integrating sphere containing a photo-cell.

Cheshire's apparatus for measuring the transmission of light by photographic lenses makes use of measurements of the brightness of the real image formed by a lens. It is shown in Fig. 3. A Nernst lamp filament A is imaged by a microscope objective B onto a small hole placed at the focus of a collimator lens C. G is the lens to be tested and H is an auxiliary lens to assist in forming an image of convenient size on the photometer cube at D. E is a matching lamp to balance the photometric field of D. All these parts are mounted on a graduated bar, so that they can be moved as necessary. The procedure is as follows: G and H are placed in their supports and H is moved until a convenient sized spot of light appears on D. E is then moved to give a balance. Let D_1 be the diameter of the entrance pupil of G (or diameter of the beam entering it, if this is less in diameter than the pupil). The light flux incident on the lens is ID_1^2, where I is a constant involving the intensity of light in the collimated beam. The flux is reduced to kID_1^2

after passing through the lens, and if it is spread over a spot of diameter d_1 on the photometer screen, the illumination there will be kID_1^2/d_1^2. This will be matched with an equal illumination from lamp E, at a distance R_1. If the candlepower of E is C, we may write:

$$\frac{kID_1^2}{d_1^2}=\frac{C}{R_1^2}. \tag{13}$$

Lens G is now removed, and similar readings are taken with lens H only in the beam. Now let D_2 be the diameter of the entrance pupil of H (or of the beam if the latter is smaller), d_2 be the diameter of the spot on the photometer, and R_2 the distance of E for balance. Then:

$$\frac{ID_2^2}{d_2^2}=\frac{C}{R_2^2}. \tag{14}$$

Eliminating I and C from these equations, we find:

$$k=(R_2D_2d_1/R_1D_1d_2)^2. \tag{15}$$

A simple but accurate method of measuring lens transmission has been devised by Dr. George Sabine of the Kodak Research Laboratories as shown in Fig. 4. This arrangement has the great advantage of avoiding the need of any measurements of dimensions, either of entrance or exit pupils, or size of spot produced, or of distances between parts of the apparatus, which naturally reduces the chance of error. The light source S is a lamp with a rather small filament; an automobile headlight bulb serves very well. A lens L_1 forms an image of the filament in the air at S'. An integrating sphere with opening CD is placed so that the entire beam is permitted to enter, and the photo-cell at one side of the sphere then gives an output proportional to the total flux entering the sphere. The illumination at S' would be:

$$E'=\pi Bk_1\sin^2\theta',$$

where

B = brightness of source S,
k_1 = transmission factor of lens L_1.

The flux passing through S' is

$$\phi'=E'Q'=\pi Bk_1Q'\sin^2\theta',$$

where

Q' = area of image S'.

If the lens whose transmission is to be measured is placed in the beam so that S' is near or at its nodal point, there will be little or no change in the position or size of S' and the only effect upon the above equation is to introduce the transmission factor of lens L_2, so that

$$\phi_L'=\pi Bk_1k_2Q'\sin^2\theta'$$

and consequently

$$k_2=\phi_L'/\phi',$$

which is simply the ratio of the meter readings with and without L_2 in place. It is only necessary to be sure that the opening CD is large enough to admit the entire beam into the sphere in each case.

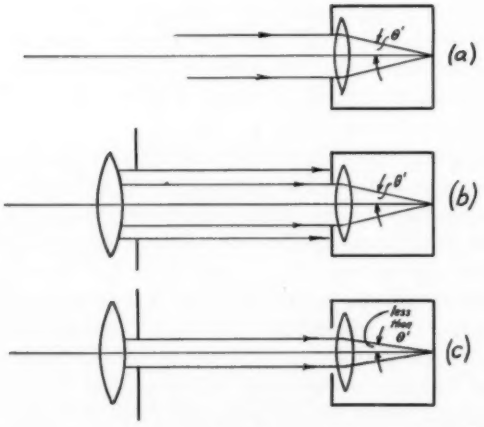


FIG. 5.

SYSTEMS OF INFINITE FOCAL LENGTH

Before proceeding to a consideration of image brightness in telescopes it will be well to consider briefly the application of our equation to the eye, inasmuch as most telescopes are used in association with the eye.

When an object is viewed by the eye, the most oblique ray to an axial image point is determined by the radius of the pupil of the eye. If this angle is θ', then the illumination on the retina is given by

$$E'=k_e\pi B\sin^2\theta'. \tag{16}$$

For simplicity we will ignore all physiological and psychological oddities of the eye and assume that the retinal illumination E' measures the apparent

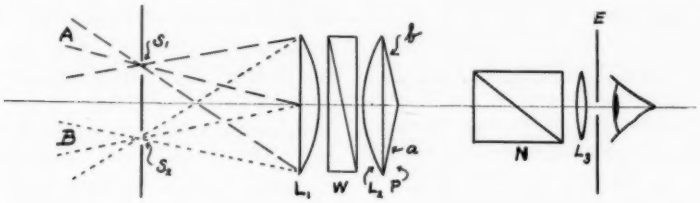


FIG. 6.

brightness B' of the object, as it appears to us. We have then

$$B' = k_e \pi B \sin^2 \theta', \tag{17}$$

where k_e = transmission factor of the eye and also takes account of the fact that the final image is formed in a medium of different refractive index from air.

Figure 5 shows the eye receiving a parallel beam of light from the eye lens of a telescope. The eye has been conventionalized as a small box with a lens and diaphragm (pupil) at the front and a receiving screen (retina) at the rear. In Fig. 5(a), the eye is looking directly at the distant object, the apparent brightness being given by Eq. (17). In Fig. 5(b), the eye has been applied to the end of a telescope having an exit pupil larger than the diameter of the pupil of the eye. In this case the eye pupil restricts the cone falling on the retina to a maximum angle of θ', and the apparent brightness is

$$B_t' = k_t \cdot k_e \pi B \sin^2 \theta', \tag{18}$$

where k_t = transmission factor of the telescope. Dividing one equation by the other gives $k_t = B_t'/B'$ or

$$B_t' = k_t B'. \tag{19}$$

From this we see that the apparent brightness of an object as seen through a telescope must be less than the brightness seen by the unaided eye by the factor k_t, and the value of this constant may be ascertained if we make arrangements to measure the apparent brightness of the object, first with and then without the telescope.

If the exit pupil of the telescope happens to be smaller than the eye pupil as in Fig. 5(c), the apparent brightness will be still less even than $k_t B'$ because of the reduction of the angle θ'.

In order to measure the light transmission of a telescope two pieces of equipment are needed:

1. A suitable radiating light source to use as an object.

2. A photometer for measuring the brightness of object and image.

In general two procedures have been used. In the first, one takes advantage of the fact that the entrance pupil is the image of the exit pupil, and vice versa. If a luminous source of uniform brightness is placed in, or near, the plane of either pupil, the image formed at the other should have the same brightness as the object, but lessened by the transmission factor. That is,

$$B_{\text{image}} = k_t \cdot B_{\text{object}}. \tag{20}$$

In the second method, the luminous object is placed at a considerable distance from the telescope and its apparent brightness as seen by the eye with and without the use of the telescope is compared.

The first method has been used by a number of workers, notably by T. Townsend Smith,[9] F. E. Wright,[10] and J. Guild.[13] Each of these workers chose as his light measuring device a Martens-Koenig polarization photometer, no doubt because of its compactness. This type of photometer is quite well known but a brief description may not be out of place.

The general arrangement is shown in Fig. 6.

Two beams whose intensities are to be compared are admitted to the photometer system through the holes S_1 and S_2. The net result effected by the lenses L_1 and L_2, the Wollaston prism W, and the bi-prism P, is that four images of S_1 and four images of S_2 are formed in plane E. These differ in polarization and position in such a way that an eye placed behind a peephole in the center of E sees the lower half, a, of the bi-prism illuminated by light from S_1 which is horizontally polarized, and sees the upper half, b, illuminated by vertically polarized light coming from S_2. The ratio of the intensities is determined by the angular rotation of Nicol prism N required to establish equality of the two fields. Lens L_3

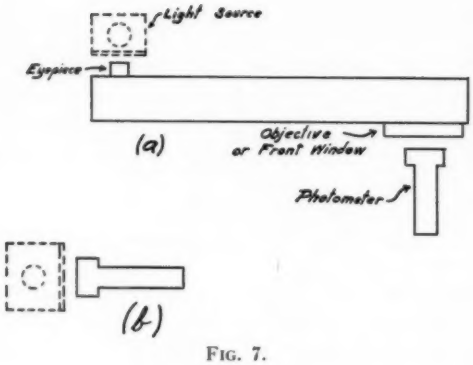


FIG. 7.

plays no part other than to assist the eye in focusing upon the surface of P.

If S_2 is permitted to view a surface of known brightness, then we may measure the brightness of any surface placed in front of S_1, as, for example, the image formed by an instrument. For convenience, a standard lamp is usually placed to one side of the instrument and light is reflected into S_2 by means of a small right angle prism. If the full field of the photometer is to be filled with light, it is necessary that the object being measured subtend at S_1 at least as great an angle as does the lower half of the bi-prism. It should be noted, however, that accurate measurements can still be made even though the field is not filled, as the photometer can be moved until even a small spot comes against the dividing line of the biprism, so that its brightness can be compared with the standard. With very small spots it becomes difficult to determine equality of the fields, however.

Figure 7 shows Guild's arrangement for measuring the transmission of a periscopic instrument.

The light source consisted of a box having a sheet of diffusing material on one side and a lamp inside. This was placed close to the eyepiece of the instrument and the photometer was placed against the objective as shown in Fig. 7(a), in order to measure the brightness of the entrance pupil. The measurement of the brightness of the source was made by placing the photometer directly against the illuminated diffuser as shown in Fig. 7(b).

The polarization photometer may give serious errors in the measurements if the light entering the instrument is polarized to any extent, as may occur if oblique reflections are encountered. To avoid such error Guild used a quarter wave plate mounted on the front of the photometer. When properly oriented, this annuls the effect of polarization of the incoming light, but has the disadvantage that the plate is of the proper thickness for only one color, so that a color filter must be used to select a rather narrow spectral region. This, of course, results in considerable loss of light and sensitivity.

Moffitt and Taylor pointed out another type of error arising in any measurement of transmission which involves setting a diffuse radiator close to either entrance or exit pupils and measuring the brightness of the other. They reasoned that light from the object is scattered and reflected from the lens mounts and instrument walls as well as transmitted, and a great deal of extra light from flare and ghosts passes through the exit pupil and is measured, thus resulting in an abnormally high apparent transmission. This effect, they found, was particularly bad when a diffuse radiator was placed close to the entrance pupil.

Their preferred method of measuring transmission was by comparison of the actual brightness of a distant object with its brightness as seen through the instrument. The object should be as small as could be worked with and it should appear on a dark field to minimize the amount of light entering the instrument.

Figure 8 shows schematically the arrangement used by them. A collimator, C, has a radiating disk of opal glass, covered by a sliding screen containing various sized holes. The smallest one which could be used was selected according to the magnification of the instrument to be tested.

The telescope under test was mounted on a platform P, which rotates about a vertical axis O. The telescope was so placed that its exit pupil

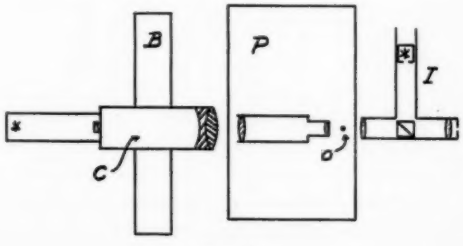


FIG. 8.

was at *O*. The photometer consisted essentially of a unit power telescope *I*, containing a photometer cube so that light from a standard source could be introduced for a comparison field. The entrance pupil of the photometer was also placed at *O*. The entrance pupil of the photometer must be smaller than the exit pupil of the telescope in order that the same sized beam of light may be picked up when the telescope is removed. The entrance and exit pupils of the photometer were about the same size, and a 2-mm hole placed at the exit pupil of *I* was the smallest stop in the system.

Pivoting of both telescope and photometer about their pupils at *O* facilitated adjustment and also permitted readings to be made on off-axis objects. Rails, *B*, were provided in order that the collimator could be displaced transversely when necessary for such purposes. To facilitate alignment of the instrument the eye peep hole could be replaced by a cap with a ground glass screen having in it a hole slightly larger than the peep hole.

A comparison was made of the entrance and exit pupil brightness method, with the method of focused images, and the latter was found to be greatly superior to the first. The first method was found to give considerable variation in the results as the distance of the radiator from the objective was changed, leaving one in doubt as to which result to accept. With the focused image method, however, very little difference in results was obtained as the distance of the source was varied between $\frac{1}{4}$ inch and 60 inches, and it was concluded that this method gave more nearly a measurement of what one wanted to know.

DISPERSING SYSTEMS

It is often important to determine the transmission factor for such instruments as monochromators, spectrometers, etc., whose principal function is the dispersal of light into a spectrum. All remarks pertaining to the other two classes of instruments are true also in this case, but some additional factors need to be considered.

In the first place it is essential that one have available a source of fairly pure monochromatic light with which to make the measurement. This could conceivably be, for example, a mercury arc with suitable filters to isolate one particular wave-length of its radiation. This would permit transmission measurements only at the particular wave-lengths corresponding to the various mercury lines. The transmission of monochromators is apt to change considerably with wave-length, however, especially in the ultraviolet, so that it is desirable to use another monochromator as a source of light of any desired wave-length.

The general procedure is to measure the flux emerging from the exit slit of the first monochromator, then let it enter the monochromator being tested, and measure the flux emerging from its exit slit. The ratio of output to input gives the transmission for that wave-length. It is, of course, necessary that the entrance and exit slits of the second instrument be large enough not to stop the beam from the first instrument, and yet narrow enough to stop out stray light.

A second difficulty is that dispersing instruments are probably more often used in the ultraviolet and infra-red than in the visible. In such cases it is impossible to see to align and focus the parts of the system, and one cannot use a visual photometer to make the measurements so that it becomes necessary to use a physical measuring instrument adapted to the wave-length used. Thermopiles have been quite generally used for this purpose. Anderson, Fraser, and Bird[59] have described a procedure of this type. Forsythe and Barnes,[60] and Kay and Barrett[45] have also contributed papers on this subject.

Thermopiles are well suited for measurements of energy at any wave-length, but have the disadvantage that their output cannot be amplified, a delicate galvanometer being required, which is subject to vibration trouble. It is also very sensitive to heat changes in its vicinity. It may not be possible to escape these difficulties in the infra-red, but for work in the visible or ultraviolet, the use of photo-cells, or photo-multiplier tubes and amplifiers would seem to offer very interesting possibilities.

Berek[61] has published a paper dealing with the theoretical aspects of the monochromator problem, but this would seem to be of more interest to the designer than to the man who wishes to use a completed instrument.

Practically all of the arrangements described in the literature using the focused image method of measurement have made use of stands or pho-

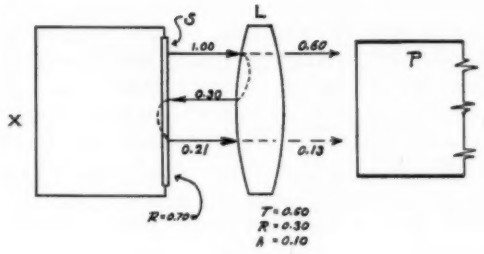


FIG. 9.

tometric benches of some sort on which the instrument could be placed, and have made use of visual photometers to measure the image brightness. There are of course, other types of visual photometers than the two types which have been described. A few writers have described photometers making use of the principle of Maxwellian view, and have adapted them for the purpose of measuring brightness of distant objects, and for the measurement of transmission. Mr. H. S. Ryland has mentioned using a method of photographic photometry in which he took photographs under standard conditions of the Ramsden disks of instruments. He also mentioned an autocollimation method in which part of the original beam of light passed twice through the instrument to be tested and was then compared with the remainder of the beam which has not passed through the instrument. Little attention seems to have been paid to photo-cells for this purpose, although they have played an excellent role in other types of light measuring instruments, particularly some of the elaborate automatic spectrophotometers, microdensitometers, etc.

A problem recently presented to the author required a device which could be used for the measurement of the transmission of some instruments of such size and weight that they could not well be transported to a darkened room, nor could they conveniently be set in place on any sort of a photometer bench. It was necessary to be able to take the photometric apparatus to the instrument, and to use it there in a well-lighted room. An instrument for this purpose has been built, but inasmuch as the details are to be published in another paper, nothing more will be said here regarding it.

ERRORS AND PRECAUTIONS

The possibility of serious error in measurements made with polarization photometers in case the light being measured is polarized to any extent, has already been mentioned in connection with the work of Guild, together with his use of a quarter wave plate to avoid the error. Moffitt and Taylor felt that this possible error was so serious as to completely overshadow the advantages of that type of photometer. One can scarcely agree with a complete condemnation of the polarization photometer, however, as it is a beautifully compact instrument, and there are many applications in which there is little likelihood of trouble from polarized light. Of course, if there is plenty of light, the quarter wave plate and its necessary adjunct, the narrow pass filter, may be employed.

One of the most serious sources of error in photometric measurements of this sort seems to have been overlooked by most of the workers already mentioned, and that is error from interreflections of light between the instrument being tested and the test apparatus. Moffitt and Taylor mentioned reflection and scattering of light as a primary source of error in using the entrance-exit pupil brightness method of measuring transmission, but it appears that they had in mind only reflections and scattering from the walls of the tube. Cuny[34] called attention to the fact that if a diffuse radiating surface is placed very close to the first lens of the system, considerable light is reflected from the system back to the source and increases the apparent brightness of the latter. Such errors, he found, could amount to as much as 20 percent if the source were not placed at a sufficient distance from the first lens. Capdecomme[41,42] found a similar error occurred when attempting to measure the reflectivity of objects under the microscope, because of the proximity of the object and the microscope objective. Confirmation of the magnitude of interreflectance errors is given by the work of Judd and Gibson,[40] who found that in measuring the reflectance of various materials, the presence of a cover glass over the sample could result in errors up to 10 percent.

The manner in which reflection effects may vitiate the results of even an apparently simple procedure such as the measurement of the trans-

mission of a photographic lens, is shown in Fig. 9. Here we have a light source X illuminating a sheet of white opal glass S. It is proposed to measure the transmission of lens L by measuring the brightness of the opal glass by means of photometer P, first viewing S directly, and then viewing it through the lens. A photographic lens might transmit about 60 percent, reflect 30 percent, and absorb 10 percent as shown. If the reflectance of the white opal glass were 70 percent, and if the lens were placed quite close to the opal glass, as is often recommended, it is not difficult to see that most of the 30 percent of the light reflected from the lens will reach the opal glass. The light re-reflected in the direction of the lens is then $0.70 \times 0.30 = 0.21$ or 21 percent of the original light. Sixty percent of this, or about thirteen percent of the original will thus be added to the light measured by the photometer. An error of 20 percent is scarcely to be permitted even in the crudest measurements. To avoid this error, or least reduce it to tolerable proportions it is necessary to have a considerable distance between source and lens, and also between lens and photometer. The light reflected by the lens is usually diverging and if the distance is large it will spread until only a small fraction of it falls upon S, to increase the apparent brightness of the source. Such precautions may be of even greater importance in more complex instruments. Failure to recognize the fact that such errors of considerable magnitude may be produced merely by bringing measuring equipment into the neighborhood of the system to be tested, constitutes a pitfall not only for the beginner but often for experienced workers.

There is prevalent an idea that insofar as questions of transmission, reflection, and absorption are concerned, the order in which light encounters the various elements of an optical system is immaterial. This is indeed true in the case of transmission. Benford[38] found in the case of a number of plane filters placed in tandem, that because of the interreflection of light between them, the light absorbed by the filters might be considerably changed by altering their order. T. Smith[20, 32] studied this problem theoretically and gave a very thorough mathematical analysis. He concluded that the expression of the photometric characteristics of an optical instrument required one transmission factor and two reflection factors, one for light proceeding forward through the instrument and one for light proceeding backwards. He might have added that two absorption factors would also be necessary. He described an arrangement in which a light source and a photometer were placed at each end of the instrument to be tested, and by making measurements using each of the four possible combinations of light source and photometer, he obtained sufficient data to calculate the characteristics of the instrument unaffected by measuring apparatus. This elaborate arrangement seems scarcely needed for ordinary purposes, but might be justified for some special purposes where one wishes to obtain accurately the separate values of the reflection and absorption factors of a system.

A simple illustration of an optical system having two quite different reflection (and absorption) factors is shown in Fig. 10. The double vertical line represents one optical system, and the single vertical line represents another, each having the characteristics shown. Incident light of intensity 1.00 is shown, and the various reflected rays have been followed through the systems with intensity values calculated as

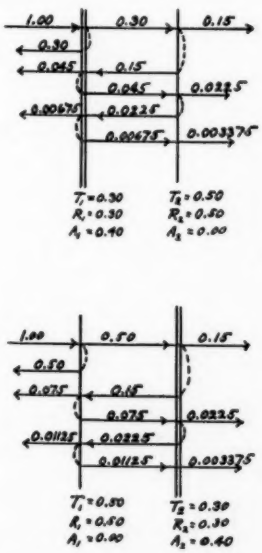


FIG. 10. In the first case $(T)=0.176$, $(R)=0.352$, $(A)=0.472$. In the second case $(T)=0.176$, $(R)=0.586$, $(A)=0.238$.

shown. Rays are shown which have suffered up to four reflections. The total reflected light (R) is the sum of the three values shown on the three arrows emerging at the left; likewise, the total transmission (T) is the sum of the values shown on the three arrows emerging at the right. The absorption (A) will be the difference between unity and the sum of reflectance plus transmission. It will be noted that in the two cases, the transmission is the same, but the reflection and absorption are quite different, the latter having twice the value in one case that it has in the other. This difference could be of considerable importance in a system where the absorbed energy is sufficient to cause heating or deterioration of filters, or other parts.

REFLECTIONS AND CONTRAST LOSS

Another aspect of the problem of repeated reflections deserves mention under a special heading. It has been shown that serious errors can be caused by reflections between measuring instrument and measured instrument, and that these errors may be minimized by keeping the light source at some distance from the entrance pupil of the instrument. Within the instrument itself there are often numerous reflecting surfaces, and one cannot quickly dispose of interreflections between them by the same method because one is seldom at liberty to increase their distances. It is, therefore, worth while to take especial note of the effects produced by such reflections.

In a photographic lens having n glass-air surfaces, each of these surfaces will reflect a small percentage of the light incident upon it back toward the object space. If this light continued back into the landscape, for example, we should not greatly bemoan its loss, but such is not the end of the matter. Each ray on its way back through the lens encounters further surfaces and at each a small, but appreciable fraction of the light is reflected and the now doubly reflected light passes through the lens to the image space. The total number of such rays reaching the object space after two reflections is $n(n-1)/2$. Each represents a curved wave front which results in the formation of an image of the original object. In general their locations are much nearer to the lens than the principal or primary image and their brightnesses are reduced from the brightness of the primary image by a factor R^2,* where R might be said to be some sort of average of the reflectivities of the various surfaces involved.

We thus find that our lens gives us one primary image, which we want, and $n(n-1)/2$ spurious images which we do not want. Each spurious image is equivalent to a very small weak source of light radiating over a definite cone angle in the direction of the primary focal plane. If one or more of these spurious images happens to be near the focal plane its cone of radiation will cut the primary image plane in a comparatively small circle, and is apt to be distinctly visible in a photograph. Such images are commonly termed "ghosts." The majority of the extra images tend to cluster in the close vicinity of the lens, as may be seen by holding a lens between a small light source and the eye, tilting the lens slightly so that one looks nearly but not quite along the axis. These images give rather large circles of illumination in the primary image plane. In a four element, air-spaced lens there are eight reflecting surfaces, so that the number of spurious images is $(8\times7)/2=28$. If such a lens is held toward a light, the images can be seen and counted, and one notices that some of the images are virtual, being located apparently between lens and object.

The fact that an image is virtual means merely that the cone of light is already diverging when it leaves the lens. It can be just as effective in sending unwanted light into the image space as a real image. The result of all this is that each small luminous area in the object is represented on the image plane by:

1. One primary image, which is the one ordinarily discussed in optics, textbooks, and

2. A series of $n(n-1)/2$ overlapping circular areas of illumination of varying diameter, most

---

* The average reflectivity of glass-air surfaces commonly encountered in photographic lenses is about 5 percent. If this be reduced to 1 percent by one of the several methods of applying low reflectance films, we can secure a gain of $5^2:1^2$ or 25 to 1 reduction in the intensity of undesired images.

Some lenses have been encountered in which one of the two reflections takes place at a highly curved surface under conditions which result in total reflection, in which case the intensity of the spurious image is R, rather than R^2. In such a case either a bright ghost or strong flare is sure to be the result and it is especially important to reduce the reflection.

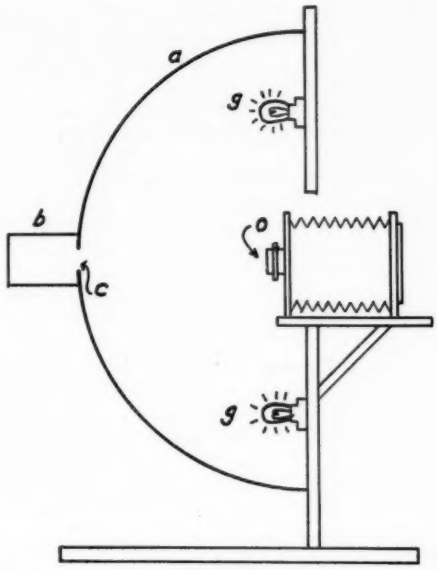


FIG. 11.

of them being fairly large. We may call these secondary images, although they are actually out-of-focus circles of diffusion.

The primary images corresponding to various elementary object areas are separate and give a faithful reproduction of the object. The secondary images, however, form a hopelessly confused jumble which results in a good deal of false illumination at various points in the image plane. The effect is particularly bad in the areas of low illumination. Two adjacent shadow areas might have brightnesses which, although low in value, still could have a ratio of say 1 : 2 and they would be quite distinguishable. If a general flare of value 4 should be added, the ratio would then be 5 : 6 and the areas would be difficult to distinguish, so that a loss of contrast is a result of general flare.

About the only extensive published work on the measurement of the contrast of lenses is contained in a monograph by E. Goldberg.[58] He arranged a microscope to travel along an optical bench with provision to rotate it about the focal point of its objective. With this he was able to measure the size and location of all of the spurious images produced by several different types of lenses. He also measured the angle of the cone of light radiated from each of these images.

To measure the contrast, he made use of the apparatus shown in Fig. 11. The lens O to be tested was mounted on a camera, and was pointed into a large hemisphere painted with a matt white paint. At the point where the lens axis pierced the hemisphere was placed a hole c, backed by a tube b, lined with black velvet. The hole c thus served as black object of zero reflectance. The contrast between c and the surrounding parts of a is practically infinite as seen directly. In the image formed by the lens, c is not black but is gray because of the flare light, and the contrast, or ratio of brightness of the images of a and c is not only finite but surprisingly small. This contrast was measured by photographic photometry.

To express the contrast numerically one may write

$$K = Ea/Ec, \tag{21}$$

where Ea = brightness of image of the zone of hemisphere a, which immediately surrounds the hole,

Ec = brightness of the image of the hole;

or may follow Goldberg and put

$$K = \log (Ea/Ec). \tag{22}$$

This was termed by him the "specific brilliance" of the lens.

It was found that if all the glass surfaces were very clean and well polished, then the value of K had rather definite values depending mostly on the number of glass-air surfaces in the lens. Table I (from Goldberg) shows this.

The presence of finger prints, grease, poor polish, and condensed moisture on a lens results in a contrast reading much lower than would be expected for the type of lens.

Chilton[44] has measured the contrast of a lens over the extent of its angular field, by moving a photo-cell across the field of the lens, but there seems to be almost nothing else published on the subject of contrast measurements. It is known that a number of workers have measured contrast from time to time but for the most part they have made no important changes from Goldberg's arrangement except to substitute a photometer for the photographic plate, and thereby not only get immediate readings but avoid the difficulties of photographic photometry.

TABLE I.

Type of lens	No. glass-air surfaces	Specific brilliance
Simple achromat	2	2.2
Double anastigmat F/6.8 with cemented lenses	4	1.8
Cooke triplet	6	1.5
Four element air-spaced lens F/6.8	8	1.2
The last with addition of a filter	10	1.0

Very little has appeared in print on the subject of contrast in optical instruments other than lenses as studied by Goldberg. Bell[12] considered the theoretical aspects of the effect of interreflections in ordinary simple telescopes and concluded that the most serious effect was the production of "ghosts" in the eyepiece. He stated that practically half of the light lost in the telescope is lost by reflection and scattering in the eyepiece, and various types of eyepiece construction with regard to their perfection in this respect. Experimental studies of contrast in telescopes and complicated instruments appear to be even more rare, however, not a single reference having been found.

BIBLIOGRAPHY

(1) H. Kruss, "Elementary explanation of illumination in optical instruments," Zeits. f. Instrumentenk. **23**, 245–249 (Dec. 1, 1902) and 254–257 (Dec. 15, 1902).

(2) H. Kruss, "Light intensity in prismatic telescopes," Zeits. f. Instrumentenk. **23**, 8–9 (Jan. 1903).

(3) R. W. Cheshire, "Transmission of visible light by photographic lenses," Proc. Opt. Convention, 34–40 (1912).

(4) P. G. Nutting, "Brightness of optical images," Wash. Acad. Sci. J. **4**, 129–134 (March 19, 1914), also Phot. J. **54**, 187–191 (April, 1914).

(5) P. G. Nutting, "Brightness and contrast in optical instruments," Astrophys. J. **40**, 33–42 (July 1941).

(6) F. Kollmorgen, "Light transmission through telescopes," Trans. Am. Illum. Eng. Soc. **11**, 220–228; Disc. **11**, 228–234 (March 20, 1916).

(7) T. Smith, "Lenses for light distribution," Proc. Phys. Soc. **28**, 211–219; Disc. **28**, 219 (June 1916).

(8) "Brightness of images in optical instruments," Bull. Bur. Stand., No. 27 (August 9, 1918); bound in volume labeled 1913–14. No author given.

(9) T. T. Smith, J. Opt. Soc. Am. **2–3**, 76 (1919).

(10) F. E. Wright, "Measurement of intensity of transmitted and reflected light by polarization photometers," J. Opt. Soc. Am. **2–3**, 65–75 (May–Nov. 1919).

(11) F. E. Wright, "Polarization photometer prisms," J. Opt. Soc. Am. **2–3**, 93–96 (1919).

(12) L. Bell, "Ghosts and oculars," Proc. Am. Acad. **56**, 45–58 (Feb. 1921).

(13) J. Guild, "Photometry of optical instruments," Trans. Opt. Soc. **23.3**, 205–216; Disc. **23.3**, 216 (1922).

(14) H. S. Ryland, "Photometry of telescopes," Trans. Opt. Soc. Disc. **23.3**, 216 (1922).

(15) C. Fabry and H. Buisson, "A universal photometer without diffusing screen," Rev. d'optique **1**, 1–12 (Jan. 1922).

(16) P. G. Nutting, "A system of photometric nomenclature applicable to optical systems," J. Opt. Soc. Am. **7**, 407–414 (June, 1923).

(17) G. W. Moffitt and P. B. Taylor, "The measurement of the transmission of light in instruments," J. Opt. Soc. Am. **8**, 511–518 (April, 1924).

(18) A. Blondel, "A modification of the Rayleigh photometer," Comptes rendus **181**, 310–312 (Aug. 25, 1925).

(19) A. Blondel, "Photometric efficiency of optical apparatus," Comptes rendus **181**, 449–453 (Oct. 25, 1925).

(20) T. Smith, "The light transmitted and reflected by a pile of plates," Trans. Opt. Soc. **27.5**, 317–323 (1925–26).

(21) S. Harcombe, "Illumination measurements in projected beams," Proc. Opt. Convention, 388–406 (1926).

(22) John W. T. Walsh, "The photometry of projection apparatus," Proc. Opt. Convention, 378–387 (1926).

(23) C. Perucca, "A photometer without diffusing screens," Zeits. f. Instrumentenk. **46**, 74–76 (Feb. 1926).

(24) A. Blondel, "Illumination photometer with Maxwellian view," Rev. d'optique **5**, 49–54 (Feb. 1926).

(25) A. Blondel, and A. Dargenton, "Apparent brightness of the face of emergence of an optical system consisting of any number of thick lenses," Comptes rendus **182**, 1443–1447 (June 14, 1926).

(26) A. Pelzer, "Influence of the illumination factor of theodolite and level telescopes upon the mean error," Zeits. f. Instrumentenk. **46**, 354–376 (July 1926).

(27) A. C. Hardy, "Brightness distribution in optical systems," J. Frank. Inst. **208**, 773–791 (Dec. 1929).

(28) V. Ronchi, "Photometric efficiency of optical systems," Nuovo Cimento **7**, 374–379 (Dec. 1930).

(29) V. Ronchi, "Photometric efficiency of an optical system," Acc. dei Lincei **12**, 663–667 (Dec. 21, 1930).

(30) H. Joachim, "Brightness of luminous surfaces formed by optical systems," Zeits. f. tech. Physik **12.3**, 133–142 (1931).

(31) J. S. Preston, "Photometer eyepiece employing Maxwellian view," J. Sci. Inst. **8**, 189–193 (June, 1931).

(32) T. Smith, "Optics of photometric measurements," Proc. Phys. Soc. **44**, 314–324 (May 1, 1932).

(33) W. S. Stiles and B. H. Crawford, Proc. Roy. Soc. B112 (1933).

(34) B. Cuny, "Source of error in measurement of transmission of optical instruments," Rev. d'optique **12**, 201–203 (May, 1933).

(35) C. H. Sharp and H. J. Eckweiler, "Photoelectric comparator for rapid measurement of reflection and transmission," J. Opt. Soc. Am. **23**, 246–250 (July, 1933).

(36) Dziobek, "Errors in telephotometry," Licht **4**, 150 (1934).

(37) F. Jentzsch and H. Funk, "Optical apparatus and methods of measurement," Die Physik **3.1**, 31–56 (1935).

(38) F. Benford, "Interface reflections between plane parallel surfaces," Gen. Elec. Rev. **38**, 277–281 (June, 1935).

(39) W. D. Haigh, "A method for the determination of the extinction coefficients of optical glasses for light in the visible spectrum," Proc. Opt. Convention, 327–346, Part I (1936).

(40) D. B. Judd and K. S. Gibson, "Effect of a cover glass in reflectance measurements," J. Research Nat. Bur. Stand. **16**, 261–264 (March, 1936).

(41) L. Capdecomme, "Role of parasite fluxes in measurements of reflecting power with a microscope," Comptes rendus **202**, 1843–1845 (June 2, 1936).

(42) L. Capdecomme, "Errors in measurement of reflectance caused by interreflections," Comptes rendus **202**, 2061–2064 (June 22, 1936).

(43) V. Ronchi, "Luminosity of telescopic instruments," Ricerca Scient. **2**, 410–425 (Oct. 1936).

(44) L. V. Chilton, "Light scatter from photographic lenses," Phot. J. **77**, 381–387 (1937).

(45) K. K. Kay and H. M. Barrett, "Transmission factor of a spectroradiometer," J. Opt. Soc. Am. **27**, 65–68 (Feb. 1937).

(46) L. Martinelli, "Luminosity of telescope images," Acc. dei Lincei **25**, 185–188 (Feb. 21, 1937).

(47) F. Benford, "Illumination characteristics of the camera lens," J. Opt. Soc. Am. **27**, 286–287 (August, 1937).

(48) R. Kingslake, "Optical problems in industrial research," J. Sci. Inst. **14**, 289–296 (Sept. 1937).

(49) L. J. Collier and W. G. A. Taylor, "Errors in telephotometry," J. Sci. Inst. **15**, 5 (1938).

(50) P. Satche, "Fundamental theorem in photometry of optical systems," Rev. d'optique **18**, 20–32 (Jan. 1939).

(51) G. Slussareff, "Brightness of the image formed by wide angle objectives," J. Phys. U.S.S.R. **4**, 537–545 (1941).

(52) John W. T. Walsh, "Principle of Maxwellian view," *Photometry* (Van Nostrand, 1926).

(53) "Light losses in optical systems," *Handbuch der Physik*, Vol. **19**, p. 511.

(54) B. K. Johnson, "Measurement of light loss in a telescope," *Practical Optics*, p. 61. (a book)

(55) A. C. Hardy and F. H. Perrin, *Principles of Optics* (McGraw-Hill, 1932), Chapter 19.

(56) L. C. Martin, *Introduction to Applied Optics* (Isaac Pitman and Sons, London, 1932), Vol. **2**, Chapter 6.

(57) H. Bouasse, *Optique et Photometrie* (Paris, Librarie Delagrave), pp. 539–543.

(58) E. Goldberg, *Der Aufbau der Photographische Bild* (1922), Part II, Chapter 3.

(59) W. T. Anderson, Jr., H. D. Fraser, and L. F. Bird, "Transmission of ultraviolet radiations by quartz prism monochromators," J. Opt. Soc. Am. and Rev. Sci. Inst. **17**, 454–462 (Dec. 1928).

(60) W. E. Forsythe and B. T. Barnes, "A quartz monochromator and its spectral transmission," Rev. Sci. Inst. **1**, 569–575 (Oct. 1930).

(61) M. Berek, "Energy relations in monochromators," Zeits. f. Instrumentenk. **56**, 109–115 (1936).

(62) Bouguer, "Traite d'Optique sur la Gradation de la Lumiere," Guerin et Delatour (1760).

(63) J. H. Lambert, "Photometria sive de Mensura et Gradibus Luminia, Colorum et Umbrae." (1760).

Optical Society of America, Incorporated

Notice of Election of Officers

IN accordance with Article III, Section 6 of the By-Laws of the Optical Society of America, the following officers and directors are to be elected at or before the Annual Meeting in October, 1943:

President, Vice President } for a term of two years.

2 Members-at-Large of the Board of Directors for a term of four years.

The present officers are:

	Term expires at annual meeting in
President—A. G. WORTHING	1943
Vice President—A. H. PFUND	1943
Secretary—ARTHUR C. HARDY	1945
Treasurer—W. W. GRAEPER	1945
Past President—K. S. GIBSON	1943
Editor—G. R. HARRISON (elected by Directors)	1945
Directors-at-Large:	
J. W. BEAMS	1943
D. B. JUDD	1945
RUDOLF KINGSLAKE	1943
D. L. MACADAM	1945
R. A. SAWYER	1945

In accordance with the By-Laws, Article III, Section 4:

"No member-at-large of the board of directors shall be eligible for re-election."

J. W. Beams and Rudolf Kingslake are not eligible for re-election.

The following Committee on Nominations has been appointed and confirmed in accordance with Article III, Section 6 of the By-Laws:

K. S. GIBSON, *Chairman*,
National Bureau of Standards,
Washington, D. C.

R. BOWLING BARNES,
Westover Road,
Stamford, Connecticut.

O. S. DUFFENDACK,
Department of Physics,
University of Michigan,
Ann Arbor, Michigan.

GLENN A. FRY,
Mendenhall Laboratory,
Ohio State University,
Columbus, Ohio.

H. KEIFFER HARTLINE,
Maloney Building, University of Pennsylvania Hospital,
36th and Spruce Streets,
Philadelphia, Pennsylvania.

It will be the duty of this committee to make nominations for the above-mentioned election. The committee report is to be made not later than July 15, 1943.

Although, after the committee has made its report, an opportunity will be given for additional nominations by petition, members are urged, as soon as possible, to suggest names which should be considered by the committee. Suggestions may be sent to the Chairman or to any other member of the committee.

Only regular, honorary, and regular-emeritus members are eligible to election. A list of members was published in the July, 1942 issue of the *Journal of the Optical Society of America*. (Later transfers to regular membership will appear in the Secretary's Report for 1942, which is scheduled for publication in the June, 1943 issue of the Journal.)

ARTHUR C. HARDY, *Secretary*

Letters to the Editor

Magnification and Brightness of Images on the Retina

FRANK BENFORD
Research Laboratory, General Electric Company, Schenectady, New York
January 12, 1943

PERHAPS every teacher of optics has had the experience of trying to convince some doubting student (who usually has had practical experience in optics) that an opera glass makes an object seem larger but never brighter. One hastens to add that the student who is impolitic enough to express his doubts has a point in his favor. The act of placing an opera glass in front of the eyes cuts off lateral illumination and the iris may then open and admit more light. But this is physiology and not optics and does not alter the case.

One peculiar feature of this question of brightness is the silence of the textbooks, and perhaps we should not be too hard on the doubter. I have seen but one reference and that one is wrong, since it states that a near object is brighter because the iris collects more light from a nearby surface!

Demonstration of the true state of affairs is not at all involved, and can be made by elementary geometrical optics. In Fig. 1 a bundle of rays along the ray axis AI converges to an image point I in the focal plane MN of the positive lens L_1 whose focal length is F. In the customary opera glass construction a negative lens L_2 of focal length f is interposed and one of the foci of this lens is also in the focal plane MN. The pencil of incident rays is refracted away from the axis and emerges as a bundle of parallel rays that enters the eye of the observer. The ray of no deviation OI gives the direction of this bundle at an angle b with the optic axis. Let the angle of the pencil before refraction be a, then we have

$$F \tan a = f \tan b$$

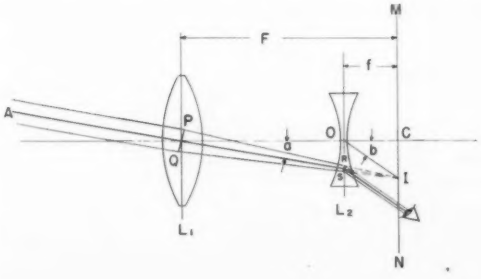
or, since a and b are small,

$$Fa = fb$$

and

$$\frac{b}{a} = \frac{F}{f}.$$

Here a and b represent the angular height of the object before and after refraction. The linear magnification is, therefore, the ratio of the focal length of the positive lens to that of the negative lens, and the areas of the two images on the retina have the ratio of F^2 to f^2.



Let us now see how much light enters into the making of these two images. If the lenses collect light at a greater rate than the increase in image area then the student is right—otherwise he is wrong.

The pencil of rays has an original diameter PQ and a diameter RS at the negative lens where the pencil again becomes a parallel bundle. RS is selected so as just to fill the iris of the eye, and this iris diameter is assumed to be constant. If the eye looks directly at the object it receives a bundle of diameter RS, but when the opera glass is used the effective bundle entering the eye has a diameter PQ. Since PQ and RS are proportional to their distances from the image point I, they are proportional to F and f. Accordingly, the light collected by the eye in the two cases is as $(PQ)^2$ to $(RS)^2$, or as F^2 to f^2. This is the identical rate of increase found for the two images and, hence, the density of light in the two is equal and they are equally bright.

In a microscope the emergent pencil may be less than the diameter of the pupil of the eye, and in this case the image seems less bright, but where the optical conditions of the figure are satisfied, either in opera glass, magnifying glass, or telescope, the equality of brightness is preserved, or as closely preserved as the surface and absorption losses will permit.

That no optical device can increase the surface brightness of an object is axiomatic to many people, but there are others who have never heard of this axiom, and to them this note is addressed, and perhaps also to their teachers.

Comment on "Meetings of Scientific Societies in Wartime"

V. G. W. HARRISON
The Printing and Allied Trades Research Association, 101 Princes Gardens, Acton, London, W.3, England
December 30, 1942

THE Editorial Comment on "Meetings of Scientific Societies in Wartime" in the October, 1942, issue of this journal has just come to my notice. From our experience over here we can certainly endorse many of the recommendations made in the memorandum to which you refer.

In the early days of the war almost all meetings of scientific societies in this country were cancelled. During the first six months of 1940, however, it became increasingly realized that public meetings were more necessary than ever in wartime in order to combat the ill effects of mental "staleness" which were affecting all scientific workers, including those engaged in urgent war work. Frequent contacts with others, the interchange of ideas and friendly criticism, are indeed the life blood of science, and the holding of regular meetings is the most convenient way of promoting them. Accordingly a few of the more enterprising societies tried arranging a few meetings, which were so well attended that others were encouraged to follow suit; and for the last two years most scientific societies have been holding regular meetings almost as

frequently as in peace time. Further, the British Rheologists' Club, the Colour Group and Optical Group of the Physical Society, and the Electronics and Industrial Radiology groups of the (British) Institute of Physics—to name only those within my personal knowledge—have all been started during wartime, largely to satisfy war needs. The success of these ventures has well surpassed the hopes of those who started them.

We have never had much difficulty in arranging meetings or in getting members' promises to attend. On account of the black-out, evening meetings in the winter have generally been avoided, though not stopped altogether. The more usual plan is to arrange a morning and/or afternoon session, with luncheon or tea, during the week. Saturday afternoon meetings are also popular, but raise difficulties for those who are busy in their gardens during the week ends "digging for victory." We have found that most employers do not hesitate to allow their employees a full day off to attend a meeting, provided that the subject matter has some bearing on their work. We do not, however, ban subjects which have no obvious relation to the war effort, provided they make a useful and original contribution to thought.

Obviously, some subjects cannot be adequately discussed at present on account of the censorship. However, with most of the subjects normally dealt with by scientific societies we have experienced no real difficulty. Neither has publication been difficult, except that, on account of the paper shortage, authors have had to condense their accounts very severly—to some, at any rate, this is useful practice.

The only time when we found it necessary to cancel meetings was during the period August–December 1940 (the Battle of Britain). Here it was necessary, not so much because members were afraid of Göring's bombs, but because transport services were in such difficulties that one's main preoccupation lay in getting to and from one's daily work.

I continue to receive notices from the O.S.A. and much regret that circumstances do not allow me to attend your meetings and to meet in person many whose names are well known to me.